Growth and high rate reactive ion etching of epitaxially grown Barium hexaferrite films on single crystal SiC substrates

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Abstract

Ferrites are an invaluable group of insulating magnetic materials used for high frequency microwave applications in such passive electronic devices as isolators, phase shifters, and circulators. Because of their high permeability, non-reciprocal electromagnetic properties, and low eddy current losses, there are no other materials that serve such a broad range of applications. Until recently, they have been widely employed in bulk form, with little success in thin film-based applications in commercial or military microwave technologies. In today’s technology, emerging electronic systems, such as high frequency, high power wireless and satellite communications (GPS, Bluetooth, WLAN, commercial radar, etc) thin film materials are in high demand. It is widely recognized that as high frequency devices shift to microwave frequencies the integration of passive devices with semiconductor electronics holds significant advantages in the realization of miniaturization, broader bandwidths, higher performance, speed, power and lower production costs. Thus, the primary objective of this thesis is to explore the integration of ferrite films with wide band gap semiconductor substrates for the realization of monolithic integrated circuits (MICs).

This thesis focuses on two key steps for the integration of barium hexaferrite (BaM-type or BaM) devices on semiconductor substrates. First, the development of high crystal quality ferrite film growth via pulsed laser deposition on wide band gap silicon carbide semiconductor substrates, and second, the effective patterning of BaM films using dry etching techniques.

To address part one, BaM films were deposited on 6H silicon carbide (0001) substrates by Pulsed Laser Deposition. X-ray diffraction showed strong crystallographic alignment while pole figures exhibited reflections consistent with epitaxial growth. After optimized annealing, BaM films have a perpendicular magnetic anisotropy field of 16,900 Oe, magnetization ($4\pi M_s$) of 4.4 kG, and ferromagnetic resonance peak-to-peak derivative linewidth at 53 GHz of 96 Oe. This combination of properties qualifies these films for microwave device applications. This marks the first growth of a microwave ferrite on SiC substrates and offers a new approach in the design and development of μ-wave and mm-wave monolithic integrated circuits. In part two, high-rate reactive ion etching using CHF$_3$/SF$_6$ gas mixtures was successfully demonstrated on BaM films, resulting in high aspect profile features of less than 50 nm in lateral dimension.

These demonstrations enable the future integration of ferrites into MIC devices and technologies.
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I would like to thank my mentor, Professor Vincent Harris, for his scientific and philosophy guidance and assistance during my graduate studies: I would not have been able to achieve my thesis without his broad and profound knowledge and his patience on me. I can only hope that my future work will reflect the enlightenment of his outstanding insight in the modern technology and in somehow repay his confidence in me.

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Chapter 1. Introduction

Ferrites are an irreplaceable group of materials used for high frequency microwave applications because of their high permeability, non-reciprocal electromagnetic properties, and low eddy current loss. Although ferrites in bulk form have been widely utilized in various types of devices, such as isolators, phase shifters, and circulators, it is still a goal of the ferrite device community to develop planar devices compatible with CMOS-based integrated circuits. A key step in the integration process is the growth of single crystal ferrite films on semiconductor substrates. Although different strategies have been attempted, most of the ferrite preparation techniques involve high temperature processing and oxygen environment which are not compatible with CMOS processing. To date, there is no ferrite thin-film based integrated microwave device obtaining any success in either commercial or military microwave market. These devices so far have offered only limited advantages over existing well-developed approaches in terms of performance, form factor, and price.

As technology advances, the urgency of miniaturization and the improvement of high frequency device performance has become more apparent. Meanwhile, many of the obstacles inhibiting monolithic integration are now diminishing due to newly available substrate materials and improved film growth techniques. Thus, the primary objective of this thesis is to explore the integration of ferrite thin film devices with wide band gap semiconductor substrates for the realization of monolithic integrated circuits (MIC).
In this chapter, we start with a brief introduction of various types of ferrites, followed by a description of different semiconductor materials as substrates. Finally, recent progress in thin film growth of ferrites, especially on semiconductor substrates is reviewed and discussed.

1.1. Ferrite materials

Ferrites are a group of magnetic oxide materials. Most ferrites “grow” in either spinel, garnet or magnetoplumbite crystal structure. The crystal structure and the atomic configuration determine their intrinsic magnetic, chemical and mechanical properties. In general, they are mechanically hard, chemically stable and have high electrical resistivity, and high permeability and high permittivity compared to other materials. Because of the low eddy current losses associated with high electrical resistivity, these materials are widely used in high frequency electronic and microwave devices. Ferrites with low dielectric and magnetic loss tangents in the frequency range from DC to millimeter wave can be readily produced. Here, we briefly discuss several key types of ferrites as well as their magnetic properties and applications in microwave devices.

1.1.1. Spinels

Spinel ferrites having the chemical formula Me$^{2+}$O·Fe$^{3+}$$_{2}$O$_{3}$, where Me represents divalent magnetic ions and Fe can be replaced by other trivalent magnetic ions, crystallize in a cubic structure. The cations occupy either tetrahedral (A) or octahedral (B)
sites and, therefore, form two sublattices. The magnetic moment of cations within each sublattice align parallel to each other and anti-parallel to the other sublattice. The normal spinel is described by the inversion parameter, $\delta$, of zero, where $\delta$ is defined as 
\[(\text{Me}_{1-\delta}\text{Fe}_\delta)^{\text{tet}}[\text{Me}_\delta\text{Fe}_{2-\delta}]^{\text{Oct}}\text{O}_4,\]
requiring that divalent metal cations occupy 8 out of the possible 64 A sites and trivalent metal ions occupy 16 out of possible 32 B sites. Typically, natural spinel materials (i.e. Fe$_3$O$_4$, CoFe$_2$O$_4$, NiFe$_2$O$_4$, etc.) assume an “inverse” structure, i.e. $\delta=1$, in which 8 divalent cations occupy B sites and 16 trivalent cations distribute equally among A and B sites. Most spinel ferrite can be classified as “mixed” in which the cation distribution is neither purely inverse nor normal but some deviation of the two. No matter which configuration, the magnetism in these structures arises from a super-exchange mechanism$^2$ and the net moment is given by the sum of individual moments of all sites. Fig. 1 shows the cation distribution in a spinel crystal structure along with corresponding magnetic moment directions.
Fig. 1. Crystal structure of spinel ferrite, with the magnetic moment direction of each cation indicated. Courtesy to Aria Yang.

The inherent flexibility of the spinel crystal structure provides opportunities for manipulating the magnetic properties by either substituting nonmagnetic cations (e.g., Zn in zinc ferrites) for the magnetic ones or by tuning the inversion of normal spinel under non-equilibrium growth.\textsuperscript{3,4} The exchange constant $J_{AB}$ is affected by such manipulations providing an effective tool for controlling material properties, such as saturation magnetization, magnetic anisotropy and Néel temperature.
In practice, spinels are successfully used in antennas, inductors, transformers, as well as electromagnetic interference suppression devices because of the high permeability compared to other ferrites.

1.1.2. Garnets

Garnets have the chemical formula $M^{3+}_3Fe^{3+}_2(O_4)_{3}$, in which $M$ is a metal of the lanthanide group, and similarly to spinels, grow in cubic crystal structure. The unit cell consists of twenty four $Fe^{3+}$ ions at tetrahedral sites (A), sixteen $Fe^{3+}$ ions at octahedral sites (B) and 24 $M^{3+}$ ions at dodecahedral sites (C). Fig. 2 shows the crystal structure of the most famous garnet, yttrium iron garnet (YIG).
Fig. 2 The crystal structure of Yttrium Iron Garnet (YIG). Courtesy to Aria Yang.

The magnetic momentons of metal ions on both B and C sites are anti-ferromagnetically aligned with respect to the ions on A sites. Garnets like YIG are easily processed with high crystalline quality. This is possibly because of all metal ions have 3+ state$^5$ and the oxygen sublattices of garnets structure are completely filled$^6$. This is demonstrated in Fig. 2. As a result, the garnet structure is most resistant to defects introduced during the material preparation and film deposition even under condition of large film mismatch with the substrate, which is a challenging problem for the growth of films of other ferrites. For high frequency applications, microwave loss is the key performance parameter and it
is determined to a large degree by the crystalline quality of the ferrite film. Not surprisingly, YIG is the most widely utilized microwave ferrite, dominating in present day commercial microwave applications.

1.1.3. Hexaferrites

As the name suggests, hexaferrites grow in a hexagonal crystal structure. It has several structural variations including M, Y, W, and Z types. BaFe$_{12}$O$_{19}$ (M type) ferrite possesses the same crystal structure as the naturally occurring mineral magnetoplumbite and it has attracted much attention in the past few decades.$^7$ Its unit cell consists of an intergrowth of structural blocks RSR*S*$_8$, shown in Fig.3.

Fig.3 Barium M-type hexaferrite unit cell structure and High Resolution Transmission Electron Microscopy (HRTEM) cross sectional image of BaM film deposited on 6H- SiC substrate. Courtesy to Aria Yang; HRTEM image, courtesy to Lena Fitting, Cornell University.
The asterisk indicates the block has been rotated by 180° around the crystal c-axis. The S block has the spinel structure with [111] direction parallel to the c-axis. The two S blocks are separated by a hexagonal R block which contains a Ba atom. The overall symmetry of the unit cell is hexagonal since it has a lower symmetry than cubic, which results in large magnetocrystalline anisotropy. The large anisotropy field found in M-type Ba-ferrite is very important for microwave device applications because of its high operational frequency. Additionally, the sole +3 oxidation state of Fe ions in BaM-hexaferrites contributes to better insulating properties compared to spinels, which provides BaM advantages over spinels in the microwave/RF applications that require low eddy current losses.

1.1.4. Microwave applications of ferrites

Ferrites have a unique nonreciprocal property which makes them key component in a wide variety of microwave devices. In these devices, the transmission or absorption of electromagnetic waves depends on the wave direction with respect to the magnetic field direction inside the ferrite. For most applications the ferrite has to be biased by an external magnetic field provided by permanent magnets. The magnets serve to saturate the ferrite as well as to make the ferrite interact with the electromagnetic wave.

Since 1990, ferrite materials and device development have progressed towards higher frequencies of operation (K- and Q-band). The zero field FMR frequency of spinel and YIG ferrites typically falls near or below 2 GHz. Using large magnetic fields to bia
YIG ferrites to operate at or above X-band frequencies is impractical. The FMR frequency is strongly dependent on the anisotropy field, $H_a$; M-type hexaferrites (e.g. BaM BaFe$_{12}$O$_{19}$) is 16 kOe, 1000 times greater than the cubic spinels. The zero field FMR frequency for single crystal Barium ferrite is near 46 GHz. Therefore, hexaferrites naturally become the material of choice for high frequency applications eliminating the need for high external biasing field as with spinel or garnet ferrites. In addition, the substitution of Fe by other cations in Ba-ferrite unit cell provides remarkable flexibility of tailoring the magnitude of the anisotropy field, and thus, the corresponding operating frequency. For example, the substitution of Sc or In for Fe reduces the anisotropy field allowing for applications from C-, X-, Ku-, K-, to Ka-bands. On the other hand, substitutions of Al or Ga increase the value of $H_a$ and allows for device applications up to U-, E-, and W-bands. Therefore, BaM hexaferrites and their substitutional companion systems can host a wide range of device applications ranging from 1 to 100 GHz.

In addition to tunability over a wide frequency band, the large magnetocrystalline anisotropy $H_a$ gives rise to a unique potential to hold an intrinsic remnant magnetization in the absence of external magnet. The remnant magnetization enables the realization of self-biased devices without the need of external magnets. For above reasons, given the advanced preparation techniques, BaM-hexaferrite is now one of the most promising ferrite materials of choice for future microwave applications in the wide frequency range of operation. In the following chapters, we will focus on the research of M-type Ba hexaferrite films on semiconductor substrate.
1.2. Semiconductors

Let us move on to another important and, perhaps, more familiar family of materials - semiconductors. Any material that has the electrical conductivity in between that of a conductor and an insulator is referred to as semiconductor. In the early 1940s, the demand for crystal detectors in radar systems motivated intensive research into the preparation of pure elemental semiconductor materials like silicon\textsuperscript{12} and germanium\textsuperscript{13,14}. This research eventually led to the invention of the junction transistor by Shockley in 1951\textsuperscript{15} and the start of the modern electronics era. Interestingly, initial semiconductor research was motivated by the requirements of developing microwaves technology. Nowadays, semiconductors are the most widely used materials in consumer, industrial and military electronics.

1.2.1. Semiconductor classes

The semiconductor family can be classified into 3 groups, which include 1) single element semiconductors like Si and Ge in the IV Group, 2) compound semiconductors like SiC in the IV –IV Group, GaAs, GaN, InP in the III-V Group, and ZnO, CdTe in the II-VI Group, and 3) alloys like Al\textsubscript{x}Ga\textsubscript{1-x}As and SiGe. Si has by far been the most dominating material since the inception of semiconductor technology, due in part to a well established fabrication technology and economic considerations. For decades driven by the massive consumer electronics market as well as efforts of thousands of engineers, the Si industry has made tremendous integrated circuit fabrication progress to realize smaller, cheaper, and faster devices from generation to generation. This progress is
accurately captured by Moore’s law\textsuperscript{16,17}. However, as Si processing (45nm) pushed to the processing limit (25nm)\textsuperscript{18} or fundamental physical limit (22 nm)\textsuperscript{19}, alternative ways other than size reduction of devices are needed for future development.

Since the discovery of semiconductors, scientists have been searching for advanced materials besides Si\textsuperscript{20}. For instance, III-V compounds like GaAs exhibiting superior electrical properties, and special optical properties that have been utilized in high frequency MMIC applications\textsuperscript{21} for some time. The use of SiGe as a replacement for classic silicon bipolar is also attracting a lot of attention\textsuperscript{22}. However, regardless of their success in some special applications, both materials suffer from limited power handling capabilities.

The ultimate semiconductor material has to meet the challenge of both high speed and high power requirements. Johnson has argued that the basic limitation on various transistor characteristics is set by the product of the breakdown electric field and the saturated electron drift velocity. The combination of these two variables which was called Johnson’s\textsuperscript{23} figure of merit (JFOM) will determine cutoff frequency and maximum power ability of the chosen material. Keys\textsuperscript{24} later suggested including another highly desirable parameter, thermal conductivity, into his figure of merit (KFOM). The properties of several semiconductor materials, along with their respective figures of merit, are listed in the Table 1 below.
In Table 1, SiC and GaN with their associated figures of merit have significant advantages over other semiconductor materials including Si and GaAs. In fact, the only material with better properties than these two is diamond, which of course, is not presently a practical material for devices in the foreseeable future.

### 1.2.2. Wide band gap semiconductor material SiC and GaN

SiC and GaN are an important group of semiconductor materials because of their wide band gap energy (above 1.7eV). The wide band gap results in better electrical and insulating properties than Si, which made these materials favorable for high frequency operation.

Take SiC for example. SiC has the tetragonal bonding between the element of silicon and carbon and has over 200 proven prototypes with different stacking sequences.

<table>
<thead>
<tr>
<th>Material</th>
<th>EB (V/cm) ×10^5</th>
<th>V_{sat} (cm/s) ×10^5</th>
<th>σT 300K (W/s)</th>
<th>K</th>
<th>Eg (eV) ×10^3</th>
<th>JFOM (W/Ω/s^2) ×10^2</th>
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</table>

**Table 1. The properties of the most common semiconductor materials.** H in 6H-SiC denotes hexagonal, C in 3C denotes cubic.
of double layers of Si and Carbon atoms. The stacking sequence determines the electronic and other properties of the crystal. We are mainly interested in 6H-SiC with its crystal structure shown in Fig. 4.

![Fig. 4. The [1,1,-2, 0] plane stacking sequence of the most common SiC prototypes.](image)

With its wurtzite structure (hexagonal), 6H-SiC has a combination of high saturated drift velocity \(2.0 \times 10^7\) cm/s), wide band gap (3.03 eV), and high breakdown electric field strength \(2.4 \times 10^6\) V/cm), which theoretically makes it an ideal semiconductor material for high-temperature, high frequency, and high-power electronics.\(^{25,26,27}\) In fact, the utilization of SiC in the circuits can eliminate the need for a
separate power amplifier which is necessary for its III-V counterpart GaAs, and IV SiGe in MMICs \(^{28}\). Additionally, the strong covalent Si–C bond provides this material with a high thermal stability and chemical inertness for unique applications in high radiation and corrosive environments.

Although the superior properties of SiC as a wide band gap semiconductor were recognized more than 50 years ago \(^{29}\), the difficulties in material preparation in terms of quality and cost prevented it from being commercially exploited similarly to Si. Until recently, the advancements in preparation techniques has reduced the cost and improved the crystal quality which allow it to be one of the prime candidates for the next generation of electronic applications.

### 1.3. Current status of ferrite film growth on semiconductor substrates

Ferrites for microwave applications were first synthesized and studied during the 1940s by Snoek’s group at Philips Laboratories \(^{30}\). These pioneering achievements inspired comprehensive investigations of the spinel, garnet and hexagonal ferrite systems. Although ferrites are successfully used in discrete elements as bulk materials, for the microwave and millimeter-wave applications, there is increasing interest in using ferrites as films rather than bulk for several reasons. First, thin films provide greater uniformity surface than bulk. Second, thin films provide lower cost, smaller size, and enhanced compatibility with planar circuit designs compared with discrete forms. Film quality, whether being polycrystalline or single crystal, is a key concern for integrated microwave
applications. The research on high quality ferrite films for microwave and millimeter-wave applications was limited and far behind the semiconductor film development. In 1970s\textsuperscript{31}, driven by rapid development of various forms of magnetic recording and bubble memory technology, the extensive work on preparing yttrium iron garnet (YIG) films was started and later extended to other ferrite films. As a consequence, YIG films became the first group of ferrite films which could be prepared to near perfect crystalline quality and applied in tunable microwave filters and magneto static wave devices.\textsuperscript{32}

In today’s technology, emerging electronic systems, such as wireless and satellite communications (GPS, Bluetooth, WLAN, automotive Radar, etc) are in growing demand, and higher frequencies of operation are needed. It is recognized that when the frequency shifts into the microwave range, the integration of microwave devices with semiconductor electronics holds significant advantages in the realization of higher performance, higher speed, higher power and smaller size devices. However, could semiconductor devices replace microwave devices altogether? Earlier researchers demonstrated an imposition of a static magnetic field on semiconductor to create magneto plasma to obtain nonreciprocity.\textsuperscript{33} MMIC active circulator based on MESFET and HEMT\textsuperscript{34,35,36} were also reported. In fact, semiconductor transmit/receive modules are widely employed in the mobile phone, and in some cases, semiconductor switches are used as replacement for ferrite phase shifters for electronically steerable phase array radars\textsuperscript{30}.

It seems that semiconductor counterpart devices will continue to be successfully utilized in some applications due to the established fabrication technology as well as
economic reasons. However, at high frequencies and broader bandwidth applications, which operate in the mm wave range up to 100 GHz, insulating materials are essential to ensure low loss propagation of electromagnetic fields. In addition, no semiconductor device has the power handling ability comparable to ferrite devices. For example, ferrite circulators have proven to be indispensable and far advantageous in the performance over any other technology. As an ultimate goal, we will explore the film-based BaM circulator integration on the wide band gap semiconductor substrate.

In the following, we will review the current status of ferrite film growth on different semiconductor substrates. Furthermore, we will discuss the potential approach of Monolithic Integrated Circuit (MIC) fabrication including recent studies on ferrite thin film processing and ferrite film patterning in efforts to realize the integration of microwave ferrite devices and semiconductor substrates.

1.3.1. Preparation of ferrite films on Si

The growth of ferrite materials on semiconductor substrates was first driven by the potential memory and recording applications. BaM for decades was considered among the top candidates for magnetic recording media because of its high anisotropy field, high coercivity, mechanical hardness, and chemical stability. For longitudinal recording, high coercivity and small grain size are highly desirable. In 1993, Sui reported that coercivity as high as 4100 Oe was achieved in the BaM film grown on Silicon by RF sputtering technique. In 1994, Hylton found that doping Cr$_2$O$_3$ can reduce the grain size down to the order of 20nm while maintaining the coercivity in excess of 4000 Oe. 

37 In 1994, Hylton found that doping Cr$_2$O$_3$ can reduce the grain size down to the order of 20nm while maintaining the coercivity in excess of 4000 Oe. 38
In contrast, when metallic alloy-based thin film longitudinal recording medium approaches the physical limit, the corresponding small magnetic grains become thermally unstable. In addition, while the recording density of metallic alloy thin film media surpasses 60 Gbits/in$^2$, the saturation magnetization reduces to below 300emu/cm$^3$, which is close to that of BaM thin film. As a result, BaM became more attractive as a candidate material for perpendicular recording medium, which requires c-axis orientation normal to the film plane. In 1985, Matsuoka reported the growth of BaM/ZnO/SiO$_2$/Si structure for perpendicular recording application.\textsuperscript{39} In 1997, Morisako reported the improvement of the c-axis orientation and the alleviation of Barium and Iron diffusion by amorphous Ba-Fe-O buffer layer.\textsuperscript{40} In 2001, Lisfi and Lodder claimed the BaM films grown directly on SiO$_2$/Si exhibit a granular structure with two easy axes (in-plane and perpendicular) and strong magnetic coupling.\textsuperscript{41} It was noticed that a ZnO underlayer promoted the orientation of the c-axis perpendicular to the film plane and a low exchange coupling was achieved by separating the grains. In 2002, Morisako reported the grain size of BaM films deposited on an AlN underlayer was suppressed to 50 nm.\textsuperscript{42} Later in 2004, He reported a better result by using Al$_2$O$_3$ as the buffer layer instead of the previous AlN.\textsuperscript{43}

For microwave applications, the deposition of ferrite films on silicon seems more challenging than for the recording industry due to the requirements of high crystal quality and c-axis orientation (normal to the film plane or in the film plane depending on the application), and greater film thickness. The crystal quality of the ferrite film directly relates to the microwave loss, which is among the most important factors to evaluate device performance at high frequency. The loss mechanism can be explained by the
ferromagnetic resonance (FMR) which stems from the dampened precession of the magnetic moments of the metal ions. Loss is closely related to the FMR linewidth. The smaller the FMR linewidth, the lower the microwave loss in its host microwave devices. Currently, it remains a great challenge to find the best ferrite film growth technique to ensure high crystal quality. In 1991, Lacroix\textsuperscript{44} proposed using SiO\textsubscript{2}, ZnO, GGG, and Al\textsubscript{2}O\textsubscript{3} as buffer layer, among them ZnO gave rise to the best BaM film orientation for \textit{in situ} crystallized barium hexaferrite films grown on Si by PLD. However, the best grown BaM film was still not suitable for LPE seed layer according to the author. In 2000, Wane et al.\textsuperscript{45} reported the growth of BaM film used for the integrated permanent magnets in MMIC circulator by e-beam evaporation. It was also reported that a layer of Au or Cu was in need to improve the adhesion of the film on Si. In 2004, Berre\textsuperscript{46} reported the growth of 10\textmu m thick BaM for passive isolator with 3.3 dB/cm of loss at 50 GHz. In 2005, Liu reported\textsuperscript{47} the growth of barium ferrite thin films by pulsed laser deposition on MgO buffered Si substrates for microwave application. Besides BaM ferrite, spinel and garnet ferrites have also been explored for the integration on silicon. In 1995, Adam\textsuperscript{48} first reported the growth of 100 micron thick YIG film on Si for the monolithic integration of an X-band circulator. The film was grown at 500°C, followed by rapid annealing at 850°C for 20 seconds. In 2004, Xi et al.\textsuperscript{49} reported on polycrystalline NiZn-ferrite films fabricated on Si (111) substrates by PLD and observed an preferential (400) orientation of the films. In 2005, Sorescu\textsuperscript{50} investigated NiZn and Zn-ferrite films deposited on silicon (100) substrates. In 2006, Calle\textsuperscript{51} et al. studied NiZn ferrite films deposited on (100) Si substrates using magneto-optical Kerr effect. In 2008, Chen et al.\textsuperscript{52-53} addressed the polycrystalline BaM films with thicknesses of 100-150 \textmu m
deposited on Al₂O₃/Si or SiO₂/Si substrates by screen printing technique. Due to a relatively low density and misalignment of grains, the BaM films exhibited large microwave linewidths that still need to be lowered to meet the requirements of practical microwave devices.

1.3.2. **Preparation of ferrite films on GaAs**

Even though it is the most dominating material in the semiconductor industry, Si has limited applications in the microwave range due to relatively high conductivity compared to other semiconductor materials such as GaAs. The conductivity translates into high loss in the form of eddy current and is not favorable for high frequency microwave applications. From this point of view, GaAs is a better candidate for use in microwave frequency. In 1987, Abe\(^54\) fabricated a microstrip junction circulator using NiZn ferrite films deposited by electro-plating and spin-spray coating onto GaAs. In 1990, Yoo and Talisa\(^55\) demonstrated the spin-spray deposition and the patterning of NiZn ferrite film on a portion of a GaAs wafer containing several MMIC circuits. For practical device applications, thick films with low losses are in demand. A 25 microns thick Ni-Zn ferrite film was achieved by a multiple deposition method with intermediate drying processes. Unfortunately, low resistivity and high dielectric loss at microwave frequencies was observed due to the poor film crystal quality. In 1995, Buhay\(^56\) reported the deposition of YIG films using high rate PLD on GaAs. The poor microwave performance (high attenuation) was explained by poor surface morphology and severe cracking of thick YIG films. In 1996, Adam\(^57\) reported the development of K-band circulators operating at 20 and 35 GHz that were monolithically integrated with both
GaAs and epitaxial GaAs-on-Si wafers. The device and its scattering parameters are shown in Fig. 5.

Despite all these efforts, no practical devices were ever achieved. As we discussed earlier, poor crystal quality of the films has a detrimental effect on the device
performance. As a matter of fact, the produced films mentioned above are mostly polycrystalline, or even amorphous, resulting in poor device performance compared with competing technologies. In polycrystalline ferrites, the impurity defects, random local anisotropy fields and residual porosity, broaden the FMR linewidth and increase the microwave loss. This is a serious obstacle, especially in circulator design and fabrication. To ensure better microwave performance, single crystal films are needed. However, successful single crystal ferrite film growth requires high temperature processing, which is beyond the tolerance of Si and GaAs substrates. In case of GaAs, even by introducing SiO$_2$ and Si$_3$N$_4$ as protective layers$^{47}$, GaAs cannot be exposed to temperatures approaching $900^\circ$C without degradation. Such temperatures, however, are required for the growth of high quality BaM films. It is well known that GaAs dissociate at $\sim400^\circ$C and silicon easily alloys under long heating. So, even the trial of a two-step deposition of BaM at temperature under $500^\circ$C, followed by annealing, was not successful in obtaining high film quality. The trial of rapid thermal annealing for several seconds also failed because it is not effective to transfer polycrystalline hexaferrite into good single crystal hexaferrites.

1.4. Monolithic integrated circuits (MICs)

In order to meet the needs of miniaturization, broader bandwidths, higher operating frequencies, and lower costs, a fully monolithic design for the fabrication of T/R modules including circulators is needed. MIC and System on Chip (SOC) approaches seek smaller, higher performance and cost-effective systems. Different to
typical ICs, MICs have both passive and active components and their interconnections fabricated on the same substrate, which is usually a semiconductor. In fact, the idea of integration of RF and passive components on the same substrate emerged soon after the fabrication of the first GaAs metal epitaxial semiconductor field effect transistor (MESFET).\(^{58}\) In 1994, a YIG/Si circulator was fabricated by bonding a 130 µm thick YIG film to a metallized Si wafer followed by the removal of the GGG substrate.\(^{59}\) Later in 2001, planar microstrip Y-junction circulators had been fabricated from metallized 130 µm thick self-biased strontium hexaferrite ceramic which was then bonded to silicon substrate to yield an integrated circulator circuit.\(^{60}\) The schematics and the microwave measurement results are shown in Fig. 6.
Fig. 6 a) Plan-view and cross-sectional schematics of the integrated circulator Circuit. GP/BL indicates the ground plane/bond layer. b) Scattering parameter ($S_{11}$, $S_{12}$, $S_{13}$) results versus frequency for an as-produced self-biased circulator circuit. The $S$ data is the dotted line. The dashed line shows transmission results when an impedance-matched microstrip line replaces the hexaferrite chip in the circuit. c) Normalized scattering parameter ($S_{21}$, $S_{31}$) results versus frequency with this circulator biased with $H < 1.5$ kOe.

Unlike the above hybrid structure, or the conventional Microwave Monolithic Integrated Circuits (MMICs) with the ferrite and semiconductor processed separately and assembled afterwards (by attaching, bonding, etc), MICs have a higher integration level providing better circuit reliability, higher power efficiency, more design flexibility, and fewer impedance matching issues. To achieve this goal of complete integration, the substrate has to be at least semi-insulating to accommodate the necessary transmission lines and passive components. The processing in addition should be based upon a planar
thin film configuration and compatible with standard semiconductor process flow. In
light of these requirements, three options are proposed to help realize the goal of complete integration:

a) To deposit high-quality ferrite films on semi-insulating semiconductor substrate
   (Si, GaAs, GaN, SiC)

b) To deposit high-quality ferrite film and semiconductor films on a mutually compatible substrate (MgO, Al₂O₃).

c) To deposit high-quality semiconductor films on ferrite substrates (YIG, BaM)

In 2003, it was reported by Ito and Ohta that GaAs⁶¹, GaN⁶², AlN⁶³, InAs⁶⁴ and InSb⁶⁵ epitaxial films were successfully grown on MnZn-ferrite substrates using MnAs buffer layers. In recent years, epitaxial films of Si⁶⁶, GaAs⁶⁷ and InP⁶⁸ grown on the GGG substrate has also been reported. Despite of these successful demonstrations, the growth of epitaxial ferrites films on semiconductor appears to be the best choice. The success of new technologies somehow depends on whether it will be adopted by the semiconductor industry. Given this reason, semiconductor substrates remain as the most popular approach for any possible integration with semiconductor devices.

In recent years, while single crystal SiC growth was fully developed, substrates have become commercial available. The successful growth of epitaxial wide band gap semiconductor films (e. g. GaN, SiC) on SiC substrates⁶⁹,⁷⁰ make SiC one of the most competitive materials for the next generation circuits. The idea of depositing ferrites on such an agile and versatile substrate arose immediately within the research community with the goal of incorporating single-crystal ferrite films into monolithic structures with semiconductors devices on the same substrate.
1.5. Thesis overview

This thesis focuses on two key steps enabling the integration of BaM ferrite devices on semiconductor substrates. First, the development of epitaxial ferrite thin film deposition via PLD on wide band gap semiconductor substrates, SiC and GaN. Second, the development of pattern transferring for BaM films using a reactive dry etching technique is demonstrated. The best grown BaM ferrite films on SiC have met the materials requirements of the microwave circulator application at the laboratory level. The reactive ion etching (RIE), based on CHF$_3$/SF$_6$ gas mixtures, was successfully demonstrated to produce sub-50nm feature sizes in BaM films at high etching rates and with high aspect profiles. Additionally, to demonstrate the feasibility of using PLD BaM films as seed layers for thick film processing using LPE, BaM film were patterned into micro-scale cylindrical pillar/pit arrays as potential seed layers. Also, deposition of thick BaM films (2-15µm) on large wafer (2 inch) was optimized for use in planar micro-inductor device fabrication. The continued development of both types of devices is ongoing.

The thesis contains six chapters. The experimental techniques and characterization of BaM films is presented in Chapters 2 and 3, respectively. In Chapter 4, the development of the BaM films on semiconductor substrates at different stages is described in detail. The self-biased MIC circulator fabrication and the essential BaM film structure patterning technique are described in Chapter 5. The primary results of the project are summarized in Chapter 6, combined with the discussion of future work to address the needs of MIC device applications.
Chapter 2. Experiment

Several different techniques can be utilized in the preparation of BaM thin films depending on the requirements of the application, including many microelectronics manufacturing techniques such as metal organic chemical vapor deposition (MOCVD)\(^{71}\), conventional chemical vapor deposition (CVD)\(^{72}\), dc or rf\(^{73,74}\) sputter deposition, electron beam evaporation\(^{75}\) and molecular beam epitaxy (MBE)\(^{76}\). In addition to vapor phase deposition, some liquid phase techniques such as Sol-Gel\(^{77}\) have also been successfully applied to BaM ferrite film growth.

Considering the wide assortment of thin film growth techniques, in this thesis we restrict our attention to pulsed laser deposition (PLD) and liquid phase epitaxial (LPE) techniques. This is mainly due to the fact that thick, high quality BaM films were previously demonstrated by PLD and LPE\(^{78,79}\). Additionally, MBE is utilized to grow (1,1,1) textured MgO buffer layers on the SiC and GaN substrates at low temperatures allowing for the heteroepitaxial PLD growth of BaM on the substrates. This step was proven necessary in order to effectively alleviate the lattice mismatch and minimize interface diffusion between the film and substrate. In this chapter, we introduce the facilities that were involved in the film growth with primary focus on the PLD system.
2.1. BaM thin film deposition by PLD

Pulsed laser deposition (PLD) is a well-established and powerful tool to grow semiconductors, dielectrics, ferroelectrics, ferrites (YIG, spinel, hexaferrite), high temperature superconducting oxides and other films with complex composition and structures. In PLD, high energy Excimer laser pulses, impinging upon a homogeneous target, produce a vapor flux, also known as a plume. The content of the plume, including ions, atoms, molecules, clusters, and other species, is condensed on the nearby substrate to form the film. The principle may seem similar to a flash evaporation technique. But, it has two major intrinsic advantages over any other conventional evaporation. First, high energy (several hundred milliJoule) transferred into the target during the short time (nanosecond) of interaction with the laser pulse can generate extremely high heating rate on a small target spot, which cause the evaporation of the target material irrespective of the evaporating point of the constituent elements. Secondly, using external laser allows deposition to take place in a reactive or inert atmosphere, depending on the composition and the stoichiometry of the desired film. These two advantages make PLD an efficient tool for the growth of stoichiometric, epitaxial, high temperature superconducting oxide films in 1987\textsuperscript{80}. In 1990\textsuperscript{81}, Vittoria et al. first proposed to grow ferrite films using PLD.

Despite the success of PLD in many applications, the growth of epitaxial BaM on wide band gap semiconductor substrates has proven challenging. Numerous unexpected challenges were encountered as research progressed. Before going into experimental details, let us first go over the basics of the PLD technique. For convenience, we separate the PLD process into four steps: ablation, transportation, deposition, and growth.
2.1.1. Ablation

Ablation is the first step of PLD processing. The physics of the complex laser–solid interaction is presently not fully understood. However, it is generally agreed that it is a far from equilibrium process. With high energy laser pulses impinging upon a small target area, part of the energy is absorbed immediately by the target material and transformed into electronic excitation energy, lattice thermal energy, and hydrodynamic energy. This complex interaction causes the target ablation, in other words, creates a dense vapor of particles extracted from the target. In addition, part of the laser energy from the pulses is absorbed by the formed vapor, which results in the increase of the vapor pressure and temperature as well. Therefore, the vapor quickly expands into the surrounding vacuum. The majority of vapor’s contents are ionized particles formed by laser-solid and laser-plume interaction. The ionized particles have been long recognized a major positive impact relative to the film growth\textsuperscript{82} and is believed critical for oxygen stoichiometry preservation in the metal oxides films\textsuperscript{83}. The high degree of ionization is indeed an important advantage of the PLD process attributed to the high energy density delivered by the laser. To examine the ionization process, consider a laser power $p$ absorbed by the target:

$$P = \frac{1}{2} \text{Re}[E \times H^*] = \frac{1}{2} c \epsilon n E^2$$

$$E = (2 \frac{P \eta}{c \epsilon})^{1/2}$$

where

$E$ = electric field in V/cm,

$P$ = power density in W/cm$^2$,  

\text{36}
\( \varepsilon = \) dielectric constant of material,
\( n = \) refractive index,
and \( c = \) velocity of light.

Take as an example a material with \( n=1.5, \varepsilon = \varepsilon_0, \) and a peak radiation power of \( 9 \times 10^8 \) w/cm\(^2\). The generated electrical field inside the target material will be \( \sim 1 \times 10^6 \) V/cm, which is sufficient to cause dielectric breakdown and the formation of the plasma.

In addition to the ions, the vapor contains many other species including photons, electrons, neutral atoms, molecules, clusters, and particulates. With regard to the film quality, particulates are the most undesirable portion of plume content. In fact, particulates “splashing” from the target are the main cause for the inhomogenous film growth, responsible for defects as well as loss of epitaxy. Typically, there are several types of splashing associating to PLD processing, which include surface boiling and exfoliation.

Surface boiling occurs when the time of energy transfer from the laser into the target is shorter than the time needed to evaporate target surface layer with thickness of material’s skin depth\(^\text{84}\). Schwarz and Tourtellotte\(^\text{85} \) estimated the maximum laser power density that a solid surface could absorb without causing subsurface boiling to be:

\[
D_{\text{max}} = \frac{252}{(\sigma f K_m)^{1/2}} \rho H_{\text{ev}} \frac{L}{t_r}
\]

where \( t_r = \) the relaxation time,
\( L = \) surface penetration of the laser,
\( \rho = \) mass density,
\( H_{\text{ev}} = \) the heat of evaporation,
\( \sigma = \text{electric conductivity,} \)

\( K_m = \text{relative permeability,} \)

and \( f = \text{frequency of the laser.} \)

From the above formula, we could expect that surface boiling is likely to take place in ablation of metal targets (high \( \sigma \)) under high power irradiation \(( \geq D_{\text{max}} )\).

The exfoliation happens when the target has a high linear thermal expansion \( \Delta L/L_0 \)
where \( L_0 \) is the thickness that is heated and \( \Delta L \) is the change in thickness caused by the laser energy absorption. Since this phenomenon probably results from the film strain, it can often be observed in high Young’s modulus materials, such as high melting metals and hard oxides.

Splashing becomes a major obstacle preventing the application of PLD technique in industry. Usually, a low laser energy density can effectively alleviate splashing at the expense of deposition rate. However, this is detrimental to the film quality as the film growth is sensitive to laser energy density. Fortunately, particulates have larger size from 0.1 to several microns and move slower (less than 50 m/s) compared with other species (100-5000 m/s) in the plume. So, one could apply a flux screening\(^{86}\) or a mechanical velocity selector\(^{87}\) technique to sieve out undesirable particulates.

### 2.1.2. Transport

In the transport phase, we discuss the phenomena involved after the interaction of the incident laser beam with the vapor in the vicinity of the target surface. It is reasonable to assume that an isothermal temperature is maintained since a dynamic equilibrium
exists between the plasma absorption and the energy transfer from thermal to kinetic. As a result, plume species obtain velocities in the range of $10^4$ to $10^6$ m/s and high energies of 1 to 100 eV, except for particulates. In the process of vapor expansion, particles’ kinetic energy is attenuated due to multiple collisions within the plume or with background gas molecules until the particles are deposited on the substrate surface. Within the plume, the frequency of particle collisions is determined by the particle size and the pressure of the background gas. It is recognized that the kinetic energy determines the particle diffusivity as well as absorption and desorption probability at the film surface. Since the kinetic energy is adjustable through ambient pressure, it provides an effective way to control the thin film growth and may be the key factor in pursuit of epitaxial growth in low temperature regime (e.g. low pressure growth). Several models, like the drag force$^{88}$ and the shock wave$^{89}$, have been proposed to calculate kinetic energy in both low and high ambient pressure environments.

In addition to the kinetic energy, species distribution is another critical factor that controls the film growth process. The expansion of the vapor containing numerous species was described by forward peaking$^{90}$ guided by the laws of gas dynamics. The shape of the expanding plume is highly dependent upon the particle density ($p$), which is described in the angular distribution form of $f(\theta) = \cos^p \theta$. For instance, a low particle density obeys the following angular distribution $p = 1$ and $f(\theta) = \cos \theta$. In PLD processing, laser energy density mainly determines the plume density, as well as the shape of the expanding plume. The target-to-substrate distance and the working gas pressure are two additional important parameters that influence the angular distribution of the plume intercepted by the substrate. Assuming unit particle absorption at the film,
surface, the angular distribution of the plume will solely determine the film thickness profile. An uneven particle distribution is detrimental to the film's uniformity, especially, in the case for large wafer substrates. As a fact, the uniformity limitations imposed by the angular distribution of particles in the plume are among the major downsides that hinder the wide acceptance of PLD as a commercial film growth tool.

### 2.1.3. Deposition:

Now, let us consider the third stage of the ablation which occurs near the substrate surface. When the energetic species arrive at the substrate, a collision region is formed between the incident flux and the desorpted atoms from the film surface. This region serves as a source for the particles condensation at the film surface. When the condensation rate is higher than the particles arriving rate, thermal equilibrium condition is met and film growth proceeds on the substrate surface fueled by the direct flow of the ablation particles. This is common to other evaporation-based film growth methods; however, the short duration of laser pulse give rise to PLD an unique effect on the subsequent film nucleation and growth. This effect can be examined by comparing the pulse duration with the mean surface diffusion time\(^9\) \((t_d)\) of arriving atoms given by:

\[ t_p = \nu^{-1} \exp\left(\frac{E_A}{k_B T}\right) \]

where \(\nu\) is the attempt frequency for atomic processes, \(E_A\) is the activation energy for diffusion, and \(k_B\) is Boltzmann’s constant. The mean diffusion time \(t_d\) determines the time scale for the atomic collision and nucleation. In PLD, for most of deposition
conditions, \( t_d \) exceeds the deposition pulse duration. As a consequence, the deposition can be seen as instantaneous for every pulse and this instantaneous deposition is followed by a relative long time interval, where no deposition takes place. During this time interval, the adatoms relax on the surface by migration and subsequent incorporation through nucleation and growth. This adatom rearrangement can be considered as an anneal process and has significant consequences in deposition, especially in alternating target laser ablation (ATLAD), which will be discussed in the later chapter.

As a matter of fact, the short duration high power density pulses give PLD another advantage of high deposition rate over other physical vapor deposition techniques. Take an example of BaM, a typical deposition rate is 0.01-0.1nm/pulse with deposition pulse duration of 10 ns. As a result, the instantaneous deposition rate can be converted to as high as \(10^6-10^5\) nm/s. This value is much higher compared to other PVD techniques whose typical deposition rates are in order of \(10^{-2}-10^{-1}\) nm/s. The instantaneous deposition rate is mainly determined by the laser energy density, target-to-substrate distance and the ambient gas properties. Additionally, the average growth rate is regulated by the pulse repetition rate and can be varied far from the instantaneous deposition rate.

### 2.1.4. Growth

Nucleation and growth is the final and the most important stage in PLD process. Nucleation occurs whenever local fluctuations from equilibrium arise in a thermodynamically stable system, which leads to a phase transition from gas to solid phase. In other words, a supersaturated gas phase is a prerequisite for the formation of
nuclei, while the formation probability is determined by the activation energy. Here, we use three different mechanisms\textsuperscript{92} to describe the process of film growth as following:

1. Three dimensional islands growth (Volmer-Weber),

2. Two dimensional full–monolayer growth (Frank-van der Merwe),

3. Two dimensional growth of full-monolayers followed by three dimensional islands growth (Stranski-Krastino).

How a substrate-film system selects the growth mode is determined by the thermodynamics of the surface energies and the interfacial energies among three phases of substrate, the condensing cluster and the vapor. This relation can be expressed in Greene’s notation\textsuperscript{93}, as

$$
\Delta G = a_1 r^2 \Gamma_{c-v} + a_2 r^2 \Gamma_{s-c} - a_2 r^2 \Gamma_{s-v} + a_3 r^3 \Delta G_v ,
$$

where $\Delta G =$Free-energy change of nucleation,

$r =$the radius of the cluster,

$\Gamma =$interface energies,

$\Delta G_v =$the change in chemical free energy per unit volume on condensation of the cluster, and

$a =$constants relate to the shape of the nuclei.

The subscripts c, s, and v refer to the condensing cluster, the substrate, and the vapor, respectively. The sign of the derivative determines the trend of cluster evolution. If it’s positive, it indicates the cluster is not stable, and will shrink on average. The negative sign in contrast implies the cluster is stable and will continue to grow. Approximately, the chemical free energy per unit volume of the cluster can be written as

$$
\Delta G_v = -\frac{KT}{\Omega} \ln\left(\frac{P}{P_e}\right) = -\frac{KT}{\Omega} \ln(1 + \xi)
$$
where \( p \) = the pressure of the arriving atoms,

\( p_e \) = the equilibrium or saturated vapor pressure of the film atoms,

\( k \) = Boltzmann’s constant,

\( T \) = absolute temperature,

\( \Omega \) = the atomic volume of the film atoms,

and \( \xi \) = supersaturation

From this definition, when \( \xi > 0 \), \( \Delta G < 0 \), nucleation starts. In other words, the volume free energy change \( \Delta G \) will be negative when the pressure of arriving atoms exceeds the equilibrium vapor pressure, i.e., an increased supersaturation. In practice, it can be made negative by increasing the deposition rate or decreasing the substrate temperature. In case of small supersaturation, the balance of the surface free energies is responsible for the film morphology.

In condition of:

\[
a_1 \Gamma_{c-v} + a_2 \Gamma_{s-c} > a_2 \Gamma_{s-v},
\]

system energy favors no bonding between film and substrate. Then, three-dimensional islands (Volmer-Weber) will form.

On the other hand, if

\[
a_1 \Gamma_{c-v} + a_2 \Gamma_{s-c} \leq a_2 \Gamma_{s-v},
\]

The system energy results in a strong bonding between film and substrate. Therefore, two dimensional full-monolayer (Frank-van der Merwe) formation will take place. This could be treated as two independent processes in which nucleation causes the formation of
surface steps and subsequent growth causes the lateral development of these steps. This condition is always self-satisfied for a perfect homoepitaxy; in general, full monolayer nucleation will be promoted by the strong film substrate bonding, low film surface energy and high substrate surface energy.

In last, three dimensional islands nucleation on two dimensional full monolayers often occurs in heteroepitaxial growth. There, the lattice mismatch between the substrate and the film will introduce biaxial strain, resulting in an increase in elastic energy. This elastic energy grows along with the increase of the layer thickness and changes the growth mode at a critical thickness, where elastic energy is comparable to the increase in the interfacial energy.

Unlike LPE and MBE, PLD is far from thermodynamic equilibrium, thus nucleation and growth are more complicated and strongly affected by the kinetic energies of the species. The theory of poly-layer growth of thin films was proposed to describe the complex film formation in the PLD process. In this theory, it is assumed that the building of a thin solid film is accomplished by the simultaneous filling of several monolayers and the supersaturation dependence can be determined by concrete model considerations\textsuperscript{95}. As a result, depending on many combined parameters, such as laser density, substrate temperature, kinetic energy, ionization degree, as well as the type of the condensing material and the physical-chemical properties of the substrate, thin films of single crystalline, poly crystalline or amorphous structures can be synthesized by PLD.
2.1.5. The NanoPLD™ System

As discussed above, PLD is a complicated processing technique. A highly efficient PLD system is required to produce high quality films. Here, the NanoPLD™ system (a PVD Inc. Product) used in the experiment will be described.

Laser:

Laser system is one of the key components of a PLD system. High output power and short pulses are one of the main requirements of PLD film growth. NanoPLD™ system is equipped with TuiLaser ThinFilmStar, which utilizes KrF gas as an excimer and produces a maximum of 250 mJ/shot at a wavelength of 248 nm. It is recognized that KrF produces the highest gain among electrically discharged pumped excimer lasers at present. In addition, the 248 nm wavelength gives rise to an efficient absorption and short penetration depth for most target materials, compared to longer wavelengths. The combination of high gain and short wavelength results in the reduction of splashing and therefore has been extensively used in PLD systems96.

Optics:

Three high quality optical elements are needed to focus and steer the beam on the target surface. In particular, one element is programmed to raster the laser beam in order to reduce the cone effect and provide a flat target surface for constant plume angle. Any beam “hot spot” and deviations from uniform ablation will produce an inhomogeneous plume and contribute to “splashing”. Therefore, the optical system, including laser optics, requires frequent and thorough maintenance. Beam alignment and other procedures were
necessary to maintain the stability of laser beam. In addition, a fused silica disk was installed behind the chamber window in order to prevent coatings on the chamber window from the plume.

**Chamber:**

The chamber was designed to allow for various PLD applications and includes a 3 target carousel for ATLAD deposition, three high-precision mass flow controllers, and a high vacuum system. As a result, ambient pressures in the range of 0.01 mTorr to 500 mTorr with reactive or inert gasses are achievable for the growth of metals, oxides, nitrides, or other materials. The rotating target holder was designed with an offset with respect to the center of the substrate to reduce the amount of particulates reaching the substrate. This design was based on the fact that heavy particulates, having a lower velocity component perpendicular to the target normal, are concentrated in the central region of the plume. The counter-rotating substrate holder is located at a distance of 5.5 cm to 9.5 cm above the target, which allows for the optimization of angular particle distribution within the plume in order to enhance the quality of the film.

Overall, NanoPLD™ is a powerful system capable of performing many predesigned deposition processes such as the tuning of cation distribution as well as doping and layered growth. However, it is mainly designed for relatively large wafers, low temperature and fast laser repetition in low pressure environments. Many of the downsides and design problems were identified, some were addressed and some still remain. For example, the offset distance of target to the center of substrate could not be adjusted in response to variant target-substrate distance and substrate diameter, therefore,
the optimization of the plume distribution can not be fully carried out. Other issues with
the utilization of rastering laser beam were discovered as well. First, the laser density will
change at the target surface responding to the change of angular between the incident
beam and target surface. As a consequence, it introduces an uneven plume distribution
relative to the substrate and therefore uneven film thickness. In addition, because the
number of pulses hitting on each target is usually different while utilizing multiple targets
in the ATLAD growth process, the laser raster range on each target is different resulting
in non-uniform composition and distortion of crystal structure. A static laser beam and
target rastering approach is preferred for complex ATLAD application as found in older
PLD systems produced by Neocera Inc.

To carry out the research described in this thesis, we upgraded the system in
several aspects to meet our requirements, such as boosting the infrared lamp power (to
increase the substrate temperature), the optimization of target-to-substrate distance (to
adjust the plume profile) and also the elevation of the laser power level (to adjust the
plume composition). These customizations were critical for the successful BaM film
growth on semiconductor substrates. The advantageous characteristics of NanoPLD™
can be described as follows:

1. Congruent transfer of the vapor species from any target to substrate surface.

2. High degree of vapor supersaturation.

4. High kinetic energy of vapor species (10-100 eV).

3. High degree of vapor ionization (30-70%).

2.2. Interface engineering by MBE

Molecular beam epitaxy (MBE) is a well matured and understood tool, which was employed here to grow a single crystal, high quality epitaxial MgO buffer layer on 6H-SiC for the subsequent BaM growth by PLD. In MBE, thin films grow by reactions between thermal-energy molecular or atomic beams of the constituent elements at the substrate surface, which can be maintained at different temperatures. This has significant advantages over other techniques to grow thin epitaxial layers in the low temperature regime. The composition of the deposited films depends on the relative arrival rates of the constituent elements, which in turn depend on the evaporation rates and sticking coefficients of the corresponding materials. The growth rate is typically low enough (lower than 2~3 Å/s) to ensure surface movement of the impinging species on the growing surface and can result in very smooth and uniform thickness films.
Chapter 3. Film Characterization

The techniques used in this thesis to characterize the prepared ferrite films will be discussed in this chapter. For those standard tools, such as X-ray diffraction (XRD) and scanning electron microscopy (SEM) used in film structural analysis, a general description of the principles will be provided. More emphasis will be placed on the important customized or home-built equipment. The technique of ferromagnetic resonance (FMR), for example, will be explained at length as related to physical principles and system setup.

3.1. Structural characterization

3.1.1. X-ray diffraction

X-ray diffraction (XRD) is an important, non-destructive technique, for structure investigation of crystalline materials. In this research, XRD was utilized to study information on structure, phase, lattice parameter, and crystal orientation of the film samples. The structure and phases of the film were determined by comparing the relative intensity and position of the peaks in the measured XRD spectrum with standard powder diffraction files (PDF). The measured XRD peaks are formed by constructive interference of a monochromatic X-ray beam (Cu Kα, wave length of 1.5418 Angstroms) scattered from each set of lattice planes (h, k, l) at specific angles. The peak intensity of a given
reflection is proportional to the number of (h, k, l) planes in the reflecting condition, as known as Bragg’s law, illustrated in Fig. 7.

Fig. 7. Illustration for XRD peak generation and calculation of d-spacing in crystals.

Simply considering an x-ray beam incident at angle (θ) on a pair of parallel planes (P₁ and P₂) separated by an interplanar spacing (d), diffraction takes place only at the condition of two waves represented by 1’ and 2’ having same phase. As a result, the difference in the path length between 1 to 1’ and 2 to 2’ must equal an integral number (n) of wavelengths, λ. The Bragg’s law may be written in the form:

\[ 2d \sin \theta = n\lambda \]

Or \[ d = \frac{n\lambda}{2 \sin \theta} \]

For a cubic structure, the lattice parameter is calculated by:

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2}}. \]
For a tetragonal structure, the lattice parameter can be calculated by:

\[ d_{hkl} = \frac{a}{\sqrt{h^2 + k^2 + l^2 (a^2/c^2)}}. \]

The measured lattice parameters can be further compared with the standard value to extract the information of stress and defects in the sample.

A c-oriented epitaxial BaM film with good quality on a semiconductor substrate is the ultimate objective. Therefore, film texture (preferred orientation) is the major concern in these XRD studies. The XRD spectrum for a perfect c-oriented BaM sample should only exhibit basal plane peaks, i.e. (0,0,2n) planes. Any other peaks would indicate the film contains crystallites with c-axis oriented away from the substrate normal direction. In texture measurements, we locate preferred planes (i.e. {1,0,0}) by choosing the 2θ angle in the source-counter setup and collect the diffraction spectra from intensities diffracted by selected planes at different positions. The results of the measurement are plotted by means of the stereographic projection and the resulting plots are referred to as pole figures, illustrated in Fig. 8.
Fig. 8. A pole figure of (100) measured for a particular direction (i.e. the normal to the (hkl) plane) where RD denotes rolling direction, ND for normal direction and TD for transverse direction. \((\alpha, \beta)\) denotes sample position when sample rotates. \(P\) is the projection of the (100) pole at this point.

Therefore, pole figures can show the statistical distribution of different crystal planes to any given direction.

### 3.1.2. Scanning electron microscope

Scanning electron microscope (SEM) utilized in this research is an Ultra-high Resolution Scanning Electron Microscope S-4800. In this system, a finely focused electron beam scanned across the surface of the sample. The incident electrons collide
with atoms in the film and then generate low energy secondary electrons, backscattered
electrons, and characteristic X-rays. The secondary electrons are collected by detectors
and form topographical images of the sample up to $x10^6$ scale. The generated X-rays are
used in energy dispersive x-ray analysis (EDX) to obtain elemental composition of the
sample.

As BaM films are essentially insulators, during SEM measurement, the electric
charge will eventually build up on the film surface. The film charging is a major concern
because it effectively reduces the energy of the primary electron beam and causes image
distortion and possible thermal damage to the film. Fortunately, these drawbacks are
circumvented in atomic force microscopy (AFM). From this point, AFM is an alternative
way to measure the surface topography along with surface roughness.

### 3.1.3. Atomic force microscopy

Atomic force microscopy (AFM) provides a measure of the surface roughness,
grain size, and grain size distribution. The system utilizes a tip on the end of a cantilever
which deflects in response to the force between the tip and the sample during the scan.
Fig. 9 illustrates the mechanics of AFM.
As the cantilever flexes while scanning the film surface, the light from a laser is reflected from the back of the cantilever into the split photo-diode. By measuring the differential signal (A-B), changes in the bending of the cantilever can be measured reflecting the surface structure of the sample. Generally, there are three main classes of cantilever-film interaction including contact mode, tapping mode and non-contact mode. The one used here is tapping mode. When operated, the cantilever is oscillated at its resonant frequency (hundreds of kilohertz) and positioned above the surface so that it only taps the surface for a very small fraction of its oscillation period. In the experiment, we measured surface profile as well as phase image. Both image contrasts is derived from material properties such as surface morphology, stiffness and viscoelasticity.

3.1.4. X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is a surface sensitive analysis technique used to determine the composition and bonding information of samples. In this method,
soft X-rays (1486.6eV from an Al anode or 1253.6eV from an Mg anode) were used to excite and eject electrons through photoemission during the interaction with atoms. The photoelectrons are collected and their kinetic energy is measured. From the measured kinetic energy and the incident X-ray energy, the electron’s binding energy is determined by the following equation.

$$E_b = h\nu - E_k - \phi,$$

where $E_b$ is the binding energy of the photoelectron, $h\nu$ is the energy of the incident X-ray, $E_k$ is the kinetic energy of the photoelectron, and $\phi$ is the work function. The work function is the minimum energy required to excite an electron from the highest occupied level into the vacuum. Since the binding energy of the photoelectron is characteristic to a specific atom regardless of incident energy and instrumentation, it can be used to identify the elements present.

In XPS, small “chemical shifts” in binding energies provide chemical state information. As shown in Fig. 10, the binding energy of Fe 2p$^{3/2}$ electrons is affected by the Fe atoms’ chemical environment. The binding energy for Fe 2p$^{3/2}$ electrons in metallic iron is around 706.8eV, whereas in case of Fe$_2$O$_3$, it is about 710.7 eV. This difference can be essentially explained in terms of simple electrostatic interactions. Fe atoms on average have fewer electrons in the Fe oxide than in the metal iron, due to the fact that the oxygen atoms tend to take part of the electronic charge from the iron atom by a polarization of the valence shells. Therefore in iron oxide, the electron-electron interaction at the iron atomic centre decreases and the binding energy of the localized electron increases.
Fig. 10. XPS spectrums of metallic iron and iron oxide, indicating different iron bonding states in different chemical environment. Courtesy to Zhuhua Cai.

A typical XPS spectrum consists of the measured electron counts over a range of binding energies. The composition of a sample can be determined by utilizing peak area or peak height fit method. The relative concentrations of different elements can be determined from relative peak intensities. Therefore, the surface chemistry stoichiometry could be obtained. With Argon etching, XPS could be used in the study of the interface properties and film depth profile, which is very important to understand the film growth mechanism.
3.1.5. High resolution transmission electron microscopy

High Resolution Transmission Electron Microscopy (HRTEM) was applied to study the crystallographic structure of BaM sample at atomic scale. As opposed to conventional microscopy, HRTEM does not use amplitudes, i.e. absorption by the sample, for image formation. Instead, it uses the phase of the electron wave to generate contrast in the image. In these measurements, the penetrating electrons were scattered by the positive atomic potentials of the atom cores and channeled along the atom columns of the crystallographic lattice. The interaction between the electron waves in different atom columns satisfy Bragg’s diffraction condition and carries the sample’s information.

Since HRTEM is a phase-contrast imaging method, it is important to realize that the recorded HRTEM image is not a direct representation of the samples crystallographic structure. For instance, high intensity might or might not indicate the presence of an atom column in that precise location. In addition, this imaging approach requires preparing sample thin enough in order to limit the image affected by electron wave amplitude variations.

3.2. Magnetic properties characterization technique

3.2.1. Vibrating sample magnetometry

Static (DC) magnetic properties were measured using the vibrating sample magnetometry (VSM). The principle of operation for the VSM is the detection of an induced dipole field from an oscillating magnetic sample. The sample is placed in a
uniform magnetic field provided by a permanent magnet or electromagnet and vibrated vertically by a loudspeaker cone.

The static magnetic properties are best described by a hysteresis loop and a magnetization curve as shown in Fig. 11.

![Hysteresis loop and magnetization curve](image)

**Fig. 11** Hysteresis loop and magnetization curve of a typical ferrimagnetic material.

The shape of the hysteresis loop is determined by the orientation of magnetic domains and the exchange energy within the material. From the hysteresis curve, three primary magnetic properties of a material can be determined:

1. The saturation magnetization ($4\pi M_s$)
2. The remnant moment ($M_r$)
3. The coercive field ($H_c$).
For very thin films, the paramagnetic or diamagnetic substrate contribution was very carefully subtracted from the measured hysteresis loop.

3.2.2. Ferromagnetic resonance

The ac magnetic properties are the most important parameters of the film for microwave device application and they are measured using the ferromagnetic resonance (FMR) technique. Typically, the FMR measurement is performed by placing the BaM film in a shorted waveguide and detecting the differential absorption signal. However, due to the complex structure of BaM/SiC and semiconducting nature of SiC substrates, we employed the resonant method to increase the signal/noise ratio.

The fundamental physics of FMR originates from gyromagnetic motion, described as:

\[
\frac{dM}{dt} = \gamma M \times H_{\text{eff}},
\]

where \( M \) is magnetic moment, and \( \gamma \) is gyromagnetic ratio, \( H_{\text{eff}} \) is the effective internal magnetic field, which is the sum of external field, shape anisotropy field and magnetocrystalline anisotropy field, and can be described as:

\[
H_{\text{eff}} = H_{\text{ex}} - H_{d} + H_{a}.
\]

When the microwave signal is introduced into ferrite thin films, with the assumption of having both external field and magnetocrystalline anisotropy field normal to the film, the FMR frequency condition may be given as:

\[
f = \frac{\gamma}{2\pi} \left( H_{\text{ex}} - 4\pi M_s + H_{a} \right),
\]
where $M_s$ is the saturation magnetization. The saturation magnetization and magnetocrystalline anisotropy field are of fundamental importance. In the absence of an external applied field, they determine the natural resonant frequency through the magnitude of the internal field. In fact, for many of these applications the ferrite has to be biased by an external field from a permanent magnet. The magnet serves to saturate the ferrite as well as to shift the FMR frequency to higher or lower frequency band required for certain device applications. In each FMR measurement, a specific fixed microwave frequency (40 Ghz to 60 Ghz) was choosen, and the external magnetic field was swept from a particular range depending on the measurement purpose.

In this thesis, low microwave loss is the most desirable characteristic for the film. This microwave loss can be described phenomenologically by the damping of the procession of magnetic moment $^{100}$.

**Gilbert damping form:**
\[
\frac{1}{\gamma} \frac{d\vec{M}}{dt} = \vec{M} \times \vec{H} - \frac{\alpha}{\gamma M} \vec{M} \times \left( \frac{d\vec{M}}{dt} \right),
\]

**Landau-lifshitz form:**
\[
\frac{1}{\gamma} \frac{d\vec{M}}{dt} = \vec{M} \times \vec{H} - \frac{\alpha}{\gamma M^2} \vec{M} \times \left( \vec{M} \times \vec{H} \right).
\]

For small damping,
\[
\alpha \approx \frac{\lambda}{M \gamma}, \text{ and }
\]
\[
\frac{1}{\gamma} \frac{dM_\perp}{dt} = 2\alpha (M - M_\perp) H
\]

The solution for the above equation is:
\[
M_\perp(t) = M - (M_\perp(t = 0))e^{-\gamma t}.
\]

For steady state measurement (FMR), we define the FMR linewidth as $\Delta H$:
\[ \Delta H = \frac{\Delta \omega}{\gamma} = \frac{1}{\gamma \tau} = 2\alpha H. \]

For a given film, \( \Delta H \) is related to the film crystal quality. Any defects and misorientated crystallites would increase the FMR linewidth and correspondingly, the microwave loss.
Chapter 4. Results

In the past two decades, PLD processing for Ba ferrite films was being studied continuously and extensively. The first BaM hexaferrite film grown by PLD was reported by Dorsey et al. in 1992\textsuperscript{101}. The highest quality BaM films made by Song et al\textsuperscript{102} achieved perpendicular magnetic anisotropy and an FMR linewidth of ~16 Oe at 60.3 GHz. This result is comparable to the best barium hexaferrite sphere ever produced\textsuperscript{103} and close to a predicted intrinsic value of 10 Oe for Mn-Doped BaM material\textsuperscript{104,105}. Other M-type hexaferrites, like strontium and lead hexaferrites (Sr-M and Pb-M), have also been studied and grown by PLD\textsuperscript{106,107}. Although these films mentioned above were limited to oxide substrates such as MgO and sapphire, these results still are valuable references for comparison in the growth of oriented single crystal BaM on wide band semiconductor substrates, like SiC and GaN.

4.1. Epitaxy growth

Our goal is to grow C-axis oriented epitaxy BaM on SiC (and GaN). Generally, epitaxy refers to the growth of an extended single crystal film on top of a single crystal substrate\textsuperscript{108}. Obviously, there are two types of epitaxy; heteroepitaxy and homoepitaxy. Heteroepitaxy refers to the case where film and substrate are composed of different materials. An example of heteroepitaxy is the PLD growth of BaM on a SiC substrate (BaM/SiC), which is the primary focus in this thesis. Homoeptaxy refers to film growth
where the film and substrate are the same material. An example is the LPE growth of BaM on a PLD grown BaM/SiC structure. The heteroepitaxy growth process is complex and full of challenges because of the incompatibilities between the film and the substrate such as lattice constants and thermal expansion coefficients mismatch.

### 4.1.1. Lattice mismatch

Lattice mismatch is defined by the difference of lattice parameters of the thin film and the substrate:

\[ f_l = \left( \frac{a_s - a_f}{a_f} \right) \times 100\% \]

where \( f_l = \) Lattice mismatch in \%, \( a_s = \) Lattice constant of the substrate, Å, and \( a_f = \) lattice constant of the film, Å. A positive \( f \) indicates the film is under tensile strain, and a negative \( f \) implies the film is under compressive strain. For example, 6H-SiC has lattice parameters of \( a=3.08 \) Å and \( c=15.11 \) Å, while that of BaM is \( a=5.88 \) Å and \( c=23.2 \) Å. The lattice mismatch between these two materials is 4.76\%, which is large and significant. However, lattice strain can be modified by use of an interlayer or buffer layer. The interlayer materials are typically chosen to have a similar crystal structure and lattice constant between that of the substrate and the film. An example here is BaM/MgO/SiC, where MgO (111) acts as an interlayer. The lattice parameter of cubic MgO (001) is \( a=4.21 \) Å and the equivalent lattice spacing in the MgO pseudo hexagonal structure is \( 5.958 \) Å (\( \sqrt{2} a \)). Therefore, the lattice mismatch between the interlayer and film is reduced to 1.33\%, see Fig. 12.
4.1.2. Thermal mismatch

Thermal mismatch originates from different thermal expansion coefficients of the film and the substrate. The film and substrate materials experience dimensional changes proportional to their linear expansion coefficient under temperature variation. Therefore, thermal mismatch induced strain emerges between the film and substrate. When thermal expansion coefficient of the substrate ($\alpha_s$) is smaller than that of the film ($\alpha_f$), the film will sustain biaxial tensile strain upon cooling from the deposition temperature to room temperature. Otherwise, the film will sustain biaxial compressive strain. The strain is proportional to the thermal coefficient difference between the substrate and film ($\Delta \alpha$) and the change of temperature ($\Delta T$). The thermal expansion coefficient of 6H-SiC ($\alpha_s$) is $4.3 \times 10^{-6} \degree C^{-1}$, and that of BaM ($\alpha_f$) is $1.0 \times 10^{-5} \degree C^{-1}$, which result in 132% thermal...
mismatch between the film and substrate. Assuming the as-deposited film cools off from the growth temperature of 925°C to room temperature, the thermal mismatch induced film lattice change is:

\[ f_s = \frac{\nabla \alpha}{\alpha_s} = \frac{(\alpha_s - \alpha_f)}{\alpha_f} \times 100\% \]

\[ \Rightarrow -57\% \times \alpha_f \times \Delta T \times a_f \approx 0.57\% a_f \]

which is only about 1/100 of the change introduced by lattice mismatch. As a result, the thermal mismatch is normally ignored. However, the lattice mismatch induced strain will fade away at certain layer thickness, and the thermal induced strain will intensify with the thickness of the film. Consequently, the thermal mismatch will result in defect, cracks and even case the film to delaminate from the substrate at a critical thickness.

### 4.2. PLD processing

Hereafter, we will focus on the film processing conditions and results. The samples were all prepared by pulsed laser deposition (PLD) from a single homogeneous pure phase BaM target. The deposition was carried out by NanoPLD™ with a KrF Excimer laser operating at a wavelength of 248 nm. Overall, each of the following conditions is crucial for the crystallization, uniformity and stoichiometry of the resulting film.
4.2.1. Substrate temperature

As one of the fundamental thermodynamic parameters, substrate surface temperature determines the adatom's surface diffusion and adhesive abilities, hence determines the growth mechanism. This effect is especially noticeable in the growth of BaM ferrite since the diffusion rates are typically low due to strong electrostatic force of ionic materials. As a result, high temperature promotes rapid and defect free crystal growth, whereas low temperature gives rise to disordered or even amorphous structures.

Previous research indicated that best quality BaFe$_{12}$O$_{19}$ films, as judged by their magnetic and structural properties, grown on MgO$^{111,112}$ and sapphire$^{113}$ were produced in temperatures range around 925$^\circ$C. In our study, we have similar results. At lower substrate temperatures, the adatoms experience reduced mobility, leading to a small-grained microstructure of film, which is lossy at microwave frequencies. Nevertheless, higher substrate temperatures often induce diffusion between the film and the substrate and in some cases form a second phase. Preliminary XPS studies support the fact that there is diffusion of Si from SiC substrate into the BaM films processed at temperatures above 1050$^\circ$C.

4.2.2. Laser power

Supersaturation, mainly determined by the deposition rate, is another major thermodynamic parameter influencing the film growth. In the case of PLD, the deposition rate was controlled by the laser power through the plume. For a given target material, the
pressure of the saturated vapor on the target surface ($P_s$) can be calculated to a first order approximation\textsuperscript{114} using:

$$P_s(T_o) = P_0 \exp\left(\frac{LM}{pR_cT_b} \frac{1-T_b}{T_0}\right),$$

and,

$$T_0 = \frac{LM}{pR_c} \ln\left(\frac{s_0}{q}\right)$$

where $L, M, p, S_0$ are target related parameters, which are the heat of sublimation, molecular weight, density, and the sound velocity of the target material, respectively. $P_0, T_b, R_c q$ are the environment pressure, the boiling temperature at this pressure, the universal gas constant, and the laser power, respectively. Theoretically\textsuperscript{115}, $P_s$ is in the order of $10^6 \text{mbar}$ at laser power, $q$, of $10^8 \text{Wcm}^{-2}$. Under this vapor pressure, deposition rate on the substrate surface could be stated by the expression\textsuperscript{116,117}:

$$R(l, T_o(q)) = 26.4 \times 10^{21} \frac{P_s(T_o)}{2nl^2(MT_o)^{1/2}} \cos^n(j_c) \cos(j_s)$$

where $l, j_c, j_s$ are geometry related parameters, representing distance between the ablation and deposition, angles of $l$ respect to the target surface and substrate surface normal, respectively; $n$ is an empirical factor between 2 and 12, which depends on the experimental conditions. From above discussion, one could see deposition rate, $R$, was mainly determined by laser power density, $q$, at a given system geometry and working gas pressure.

The laser power density, in addition, associates with high kinetic energy of the plume. The presence of high energy species in the plume may result in lower crystallization temperatures or denser film structures for a given temperature. However,
high enough energy species may also cause damage to substrate, which in turn inhibits the epitaxial film growth.

From the above discussion, laser energy density should be increased from the threshold to a proper level in an effort to produce abundant ionized species having high kinetic energies. In our experiment, the optimum laser shot energy was determined to be 280 milliJoule.

4.2.3. Oxygen pressure

The use of oxygen during ablation has proven necessary for the preservation of oxygen stoichiometry in the BaM films. Additionally, as a background gas, it will scatter, attenuate, and thermalize the plume, therefore changing the spatial distribution, deposition rate, and kinetic energy distribution of the depositing species. When oxygen pressure is raised to a certain value, plume angular distribution is perturbed by additional particle collisions described by \( f(\theta) = \cos^p \theta \). As a result, the angular distribution will broaden and the film deposition rate will decrease. The relationship can be approximately described by \( R(\theta) \propto \cos^{p-3} \theta \). High enough oxygen gas pressure will significantly reduce the kinetic energy of the species, which is critical to the film growth. After extensive experimental study, we confirmed that, in our system at oxygen pressure of 200 mTorr, there is large number of molecule collisions of the evaporated target materials. These collisions reduce both the deposition rate and the kinetic energy of the species in the ablated plume. The quality of the resulting film is considerably worse than the film deposited at lower pressure. Our best film was produced at 20 mTorr oxygen pressure,
which is far from those reported by others.

### 4.2.4. Laser frequency sequence

PLD process consists of periodic bursts of high speed growth followed by relatively long periods of uninterrupted surface relaxation. The effects of this cyclical process, relative to those of the equivalent steady-state process, was decisive to film quality, especially when the duty cycle time is close to the time constants for all the relevant diffusion, agglomeration and dissociation phenomena. Theoretically, this may give rise to smoother film by inhibiting the nucleation of a second monolayer of islands on top of the first layer. However, for some alternating targets laser ablation deposition (ATLAD) work, long intervals between laser pulses have an adverse effect on the film structure and phase due to this nucleation and annealing cycle, resulting in deviations from the designed structures and the cation distributions.

In this work, the optimum laser repetition was chosen that allows adequate relaxation between pulses to promote the growth of the desired phase and orientation. At the same growth condition, the film quality degraded considerably when the laser repetition rate was faster than 24 Hz. Also, under the condition of having adequate relaxation time, we prefer fast repetition rate of laser pulses to reduce the complete growth time in an effort to minimize the interface diffusion between the film and substrate. In practice, each film growth started at a low deposition rate with laser trigger frequency of 2 Hz. Then the repetition rate was gradually increased to 16 Hz for a longer duration deposition.
4.2.5. Target-substrate distance

In the presence of oxygen gas, target-substrate distance has significant effect over the deposition rate and kinetic energy of adatoms. It is correlated with the mean free path of a particle in the specific background gas pressure. The particle mean free path is roughly \( \frac{K_BT}{\sqrt{2\pi d^2P}} \), where \( K_B \) is Boltzmann constant, \( p \) is the gas pressure and \( d \) is the particle diameter. When target-substrate distance is larger than the particle mean free path, multiple collisions occur, and the growth mechanism will change significantly. To minimize this effect, the distance could be chosen to be shorter than mean free path. However, if made too short, the plume distribution will be changed by strong back scattering from the substrate. In our system, constrained by other limitations of the chamber design, especially the substrate temperature requirements restrained by the heating elements, we chose the optimum target-substrate distance for the BaM film growth at 7.5 cm. However, this parameter can be varied depending on specific application requirements, such as film deposition on large wafers.

4.2.6. Target treatment

Target treatment is a big issue for many PLD applications. It is recognized that during the experiment, the laser target ablation is not a layer by layer ablation. Typically, surfaces respond to laser irradiation as periodic structures such as ripples, ridges, and cones.\(^{119}\) This irregular rough surface will affect the deposition by steering the plume at oblique angles to the substrate normal. In some cases, modified target surfaces show compositional variation due to resolidification of different components with different
melting points. The target we used has a high density and the elements have similar melting point. Furthermore, programmed rastering of the laser beam on the target surface causes minimal surface modification. As a result, we do not observe any severe irregular structures formation or compositional variation. Therefore, the need for target resurfacing was shown to be unnecessary.

4.2.7. Substrate treatment

Substrate treatment is the last step described in this section. Although, it has no direct impact upon the growth mechanism, it is very important for the success of high quality film growth. In any deposition, substrate surface defects, such as atomic steps, point defects, and line defects, generate low energy sites at which nucleation occurs preferentially. Therefore, the substrate surface quality and the surface treatment prior to deposition are critical to the growth of high crystal quality films.

In our case, different surface preparation techniques were explored, including both wet chemical and dry etch procedures. In the wet chemical etch preparation, standard semiconductor cleaning processes were employed including the exposure to boiling $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$, $\text{HF} + \text{H}_2\text{O}_2$, $\text{HCl}+\text{H}_2\text{O}_2$ acids followed by rinsing step with deionized water. The dry etch process was carried out using ion beam bombardment with Ar gas in a Kaufman-type ion source operating between 500-1000 eV. This process removed several atomic layers of the substrate by sputtering and was followed by hydrogen gas treatment to hydrogen terminate the surface.

The effectiveness of substrate surface preparation showed a significant impact on the quality of the Ba-hexaferrite films deposited under similar conditions. It was
determined that substrates prepared by ion beam bombardment had the best results, exhibiting the lowest coercivity, and a well-defined uniaxial magnetic anisotropy. Under same growth condition, the film grown on wet chemical preparation substrate had a moderate film quality, comparatively. In contrast, film grown on unprocessed substrate shows the poorest film quality.

4.3. BaM ferrite film grown on SiC

The SiC substrates used here were acquired from Cree Inc. and are commercial n-type 6H-SiC with the electrical resistivity of ~0.02 Ω-cm, and lattice parameters of a=3.08 Å and c= 15.11 Å. As discussed in the previous chapter, to grow epitaxial BaM on selective wide band gap semiconductor substrates is not straightforward and full of challenges. As a matter of fact, the large incompatibility of the substrate and film was not the biggest obstacle. Instead, maintaining a perfect starting surface was a major challenge. SiC readily experiences the formation of a native surface oxide which especially happens at high temperature and oxygen pressure. This resulted in the loss of the hexagonal template necessary for epitaxy growth. Therefore, efforts were focused on the manipulating starting surface. We will discuss these below.

4.3.1. BaM/SiC Generation I (GEN-I)

In the first series of film deposition, the film was directly deposited on the SiC substrate. The Excimer laser used operated at 248 nm wavelength with pulse energies varied from 300 to 400 mJ. The substrates were maintained at 850°-925 °C during
deposition. In each growth cycle, the laser pulse repetition rate was controlled to begin at 1 Hz leading to a low deposition rate, and then increased to 5 Hz. A series of films were deposited at oxygen pressures ranging from 1 to 400 mTorr under the same substrate temperature. After film deposition, each sample was cooled to room temperature at a negative ramp of 6 °C per minute. A post-deposition thermal treatment was implemented by two flash annealing cycles in which the substrate at temperature was ranged from 950 °C to 1150 °C in air.

All the films produced under the above conditions, show a clear hexagonal crystal x-ray diffraction pattern. A representative X-ray diffraction θ–2θ pattern, for the film processed at 20 mTorr, is plotted in Fig. 13. The diffraction peaks are indexed to the hexagonal indices (0, 0, 2n) having space group P6/mmc indicating the epitaxial growth of c-axis textured film sample.

![X-ray diffraction pattern for Ba-hexaferrite (M-type) film grown at 20 mTorr oxygen pressure. All significant diffraction features are referenced to (0,0,2n) indices having space group P6/mmc. (SH denotes substrate holder.)](image)

Fig. 13. X-ray θ–2θ diffraction pattern for Ba-hexaferrite (M-type) film grown at 20 mTorr oxygen pressure. All significant diffraction features are referenced to (0,0,2n) indices having space group P6/mmc. (SH denotes substrate holder.)
An AFM image is displayed in Fig. 14 for the sample grown at 20 mTorr of oxygen pressure. At low oxygen pressures, the images illustrate large hexagonal grains (typically 0.5 µm in diameter) with their c-axes oriented normal to the film plane confirming the epitaxy film. However, at higher oxygen pressures, we did not see clear hexagonal crystal grains in the AFM images.

![AFM image](image.png)

**Fig. 14.** Atomic force microscopy images processed in tapping mode illustrating hexagonal crystals oriented with c-axis perpendicular to the film plane.

Magnetic hysteresis loops, $4\pi M_s \text{ (G)}$ vs $H_{app}$ (Oe), for films deposited at 20 mTorr and 200 mTorr oxygen pressure are presented in Fig. 15 (a) and (b), respectively. In these data, one observes that the easy magnetic axis is aligned perpendicular to the film plane, and the hard axis aligns in the film plane. The hysteresis loops along easy axis are sheared due to the effects of the demagnetizing energy.

![Hysteresis loop](image.png)
Fig. 15. Hysteresis loops obtained by vibrating sample magnetometry of films grown by PLD at: a) 20 mTorr and b) 200 mTorr oxygen pressure.

We plot the magnetization as a function of processing oxygen pressure in Fig. 16. At low oxygen pressures, the structure of the growing film is prone to anion defects that lead to a reduction in the superexchange interactions and subsequently a reduced magnetization (see Fig. 16 for $p_{ox}$<20 mTorr). The magnetization increases to near its bulk value when $p_{ox}$~20 mtorr, signaling a reduction in anion defects. At pressures greater than 20 mtorr, the magnetization is reduced again from the bulk value. Under high pressure conditions, we suspect that the adatom mobility is reduced due to the loss of kinetic energy by collisions within the plasma. This reduced mobility results in cation disorder and trapped voids. AFM and SEM images of films grown at high oxygen pressure confirmed this speculation with signs of increased porosity, which may explain the reduced magnetization.
In addition to saturation magnetization ($4\pi M_s$), the dc magnetic properties of particular importance are coercivity ($H_c$), squareness ($M_r/M_s$) and anisotropy field ($H_a$). In Fig. 17 and 18, the coercivity and loop squareness are plotted as a function of oxygen pressure during film growth. As the oxygen pressure is increased, the coercivity is seen to increase following a power law dependence (i.e. $r^n$, $n=0.18$).
Noticeably, low coercivity and high magnetization correlate to moderate to low squareness. The low squareness is the result of the demagnetization energy. Hysteresis loop squareness, see Fig. 18, shows a similar trend as coercivity reaching a value of 0.7 at $p_{ox}=300$ mTorr. The squareness increased with oxygen pressure decreasing to at 20 mtorr.
The anisotropy field is estimated as the linear extrapolation of the hysteresis loop along hard axis to the saturation region of the easy axis loop. In this case, the anisotropy field is approximated to be \( -16 +/ - 1 \text{ kOe} \), comparable with the bulk BaFe\(_{12}\)O\(_{19}\) value of 17 kOe.\(^{121}\)

The fine grain microstructure observed in AFM images together with the high hysteresis loop squareness may account for the broad FMR linewidth (\( \sim 2000 \text{ Oe} \))\(^{122}\). This is an interesting phenomenon that may suggest a scheme for processing high quality low loss hexaferrite films. One must effectively obstruct domain walls, increasing the coercivity, and maintaining high loop squareness, while simultaneously maintaining high crystal quality to reduce microwave losses.
4.3.2. BaM/SiC Generation II (GEN-II)

Generation I was optimized at a substrate temperatures of 910°C, oxygen pressure of 20 mTorr, and laser energy of 280 mJ/shot. Based on these results, we realized that the initial growth remained as the key problem for successful film growth. Even with perfect substrate surfaces, SiC and BaM still have a 4.76% lattice mismatch, which is expected to introduce in-plane stress creating copious stacking faults and assorted lattice defects. Furthermore, we found GEN I samples suffered severe interface diffusion from x-ray photoelectron spectra (XPS) depth profile studies. To address these challenges, we developed the second generation GEN II samples grown by PLD.

Our first attempt was to introduce a pure MgO buffer layer. However, we found the films have poor uniaxial magnetic anisotropy. This led us to focus on processing schemes intended to mediate the strain and diffusion across the film-substrate interface. To this end, we adopted the practice of using a thin graduated MgO multilayer in the early stages of film growth. The multilayer structure consists of MgO layers interwoven with BaM layers, shown in Fig. 19. This structure can be represented by \([\text{MgO}(A)/\text{BaM}(B)]_n\) where \(A\) is the thickness of the MgO layer, \(B\) is the thickness of the BaM layer, and \(n\) is the number of repeats. The layer thickness (\(A, B\)) is controlled by the number of laser pulses or shots incident upon each target (\(A’, B’\)). The first \([\text{MgO/BaM}]\) layer is the thickest, at \(A’=80\) shots and \(B’=150\) shots. Subsequent repeats have the MgO layer reduced by 10 shots. After 9 periods the MgO growth is terminated and a thick BaM layer (~ 500 nm) is then grown. A
single laser shot provides ~ 0.01 nm of MgO and BaM, respectively. In this growth scheme the interfacial region of the film exists as a layered and possibly alloyed structure.

**Fig. 19. Illustration of MgO/BaM interwoven multilayer practiced to mediate the film strain in GEN-II sample growth.**

Films grown with the gradual buffer layer demonstrated superior uniaxial magnetic properties to those without this modification. For the highest quality films, we measured the squareness as low as 0.2. It is typical for hysteresis loop squareness values to track as the inverse of crystal quality metrics such as FMR linewidth.\textsuperscript{123} XPS depth profiling measurements show that this modified layer provides a barrier to the diffusion of Si into the BaM film. Compared with the GEN-I samples, the GEN-II films grown via this approach were found to have better orientation and much less interface diffusion between the deposited BaM film and SiC substrate. As a result, the ferromagnetic resonance linewidth of GEN-II samples was reduced to 500 Oe from 1200 Oe, without post-deposition annealing.
X-ray $\theta$-$2\theta$ diffraction measurements using Cu K\textalpha{} radiation (see Fig.20) reveal (0, 0, 2n) diffraction peaks consistent with a pure phase magnetoplumbite crystal structure with strong c-axis orientation perpendicular to the substrate plane.

![X-ray diffraction pattern](image)

**Fig.20.** X-ray 0-20 diffraction pattern for Ba-hexaferrite (M-type) film. All significant diffraction features are referenced to (0, 0, 2n) indices having space group P6/mmc. (SH denotes substrate holder)

Atomic force microscopy (AFM) images, Fig. 21, show 0.5-1 $\mu$m diameter grains, with no signs of smaller grains as observed in GEN-I films. The crystallites appear to be densely packed and have their basal planes aligned parallel to the plane of the substrate. Upon close inspection one sees that the basal planes are terraced which may result from the layer-by-layer growth of the crystallites. This morphology may also result from crystal nucleation at skew dislocations on the surface of the SiC.
Fig. 21. Atomic force microscope image processed in tapping mode illustrating hexagonal crystals oriented with c-axis perpendicular to the film plane.

The anisotropy field is estimated of ~16+/1 kOe from the hysteresis loops, in Fig.22, which is in reasonable agreement with the bulk BaFe$_{12}$O$_{19}$ value of 17 kOe.

Fig.22. Hysteresis loop obtained by vibrating sample magnetometry with a maximum applied field of 12,500 Oe aligned parallel (dashed) and perpendicular (solid) to the film plane.
In this study, we further optimized the laser frequency condition during deposition, in order to enhance adhesion and epitaxy at the interface. Laser repetition rate was slowly raised from 2 Hz to 16 Hz for the first 5 minutes, and then fixed at 16 Hz for the remaining 30 minutes of growth.

4.3.3. BaM/SiC Generation III (GEN-III)

The magnetic properties of the GEN-II samples improved substantially with the introduction of interwoven MgO/BaM multilayers at the film-substrate interface compared with GEN-I samples. Post-deposition heat treatments were found ineffective in further reducing the FMR linewidth from 500 Oe. Therefore, a new technique to improve the interface layer was in demand.

Theoretically, an MgO buffer layer is perfect to reduce the lattice mismatch between the BaM and the SiC from 4.76% to 1.33%. However, the use of a PLD-grown MgO buffer layer did not substantially improve the magnetic quality of the films owing to high porosity and less than optimal crystallite orientation. This could be explained by the quick oxidization of SiC during the PLD ablation in a high temperature (910°C) oxygen environment. Since, MgO (111) epitaxy films could be deposited at ~150 °C on 6H-SiC by MBE\textsuperscript{124}, we choose to prepare MgO (111) layer on SiC substrates using MBE.

In MgO growth, the oxygen plasma was held constant at 100 W and the chamber pressure at 5×10\textsuperscript{-6} Torr. The Mg:O flux ratio was ~1:20 which resulted in single crystal MgO films that grew conformal on the 6H-SiC\textsuperscript{131}. After MBE growth of the MgO template, the sample was immediately transferred to the PLD chamber for the Ba-M growth. VSM results of the as-deposited BaM are shown in Fig. 23. The hysteresis loops
confirm that the easy magnetic axis of the BaM film is aligned perpendicular to the film plane. This is consistent with the crystallographic c-axis aligning perpendicular to the sample plane and is the desired orientation for conventional microwave Y-junction circulator device applications. The estimated anisotropy field, 16.9 ± 0.2 kOe, is in agreement with the published results of the single crystal BaFe$_{12}$O$_{19}$ value of 17 kOe. In addition, the 4.1±0.3 kG magnetization of the film compares well to the bulk value of 4.48 kG. XPS depth profile of the as-deposited film showed substantially less diffusion occurred in the BaM film, and little Fe diffusion occurred in the bulk SiC. Atomic force microscopy (AFM) revealed a smooth surface (1.3 nm root-mean-square roughness over a 2 μm square) with indications of layered growth of the as-deposited film.

Fig. 23. Hysteresis loop obtained by vibrating sample magnetometry with a maximum applied field of 12,500 Oe aligned parallel (dashed) and perpendicular (solid) to the film plane. The sample had been optimally annealed (see text). The perpendicular $4\pi M_s$ of 4.4 kG compares well to the bulk BaM value of 4.48 kG.
To fully characterize the texture of the BaM film, pole figures were obtained by tilting the sample and rotating it in a spiral pattern for a fixed value of $\theta$. The angle between the film normal and the line bisecting the incident and detected x-ray beams ($\varphi$) was varied from $0^\circ$ to $85^\circ$ and the azimuthal angle about the bisecting line ($\psi$) was varied from $0$ to $360^\circ$. In this work, pole figures were obtained for $\theta$ values of $23.03^\circ$, $17.8^\circ$, and $30.3^\circ$, which were chosen to bring the $<006>$, $<101>$, and $<001>$ planes, respectively, into Bragg orientation (JCPDF #84-0757). The pole figure for the $<006>$ reflection, which clearly illustrates a single dominant peak and six weaker peaks exhibiting hexagonal symmetry of the as-deposited film, is illustrated in Fig. 24. The center of the pole figure corresponds to the values $\varphi = \psi = 0^\circ$. $\Phi$ is proportional to the radial distance from the center of the pole figure ($0^\circ < \varphi < 90^\circ$) and $\psi$ is the circumferential angle ($0^\circ < \psi < 360^\circ$). The intensity observed in Fig. 24 can be consistently indexed by assuming virtually all of the grains are oriented with their easy axis within only a few degrees of the sample normal. The single dominant peak about $\varphi = \psi = 0^\circ$ corresponds to the $<006>$ reflection which is consistent with the $\theta$–$2\theta$ data of Fig. 24 and is indicative of low c-axis dispersion. The six weaker peaks with hexagonal symmetry correspond to the $<104>$-type reflections which exhibit a d-spacing very close to that of the $<006>$ peaks ($2\theta = 23.018^\circ$ for $<006>$ as compared to $2\theta = 23.225^\circ$ for $<104>$). The interplanar angle between the $<104>$-type and $<006>$-type planes is $\sim 48.9^\circ$ as measured from the pole figures. This value agrees well with the expected interplanar angle of $48.6^\circ$ which can be estimated using the literature values of the lattice parameters, namely, $a = 0.5892$ nm and $c = 2.3183$ nm.\textsuperscript{125} Because the $<104>$-type reflections are observed as well defined peaks, rather than a ring, a strong epitaxial relationship between the BaM and the MgO buffer layer is confirmed.
After deposition, the BaM films were annealed in air at 1050 °C in two steps of two-minute duration each. After annealing, the saturation magnetization increased from 4.3 kG to 4.4 kG with a ΔH of 96 Oe. Figure 25 presents the XRD spectrum of the as-deposited film with a segment of the XRD spectrum corresponding to the post-anneal film as the inset to the figure. The as-deposited spectrum reveals all (0, 0, 2n) diffraction peaks indicating a pure phase magnetoplumbite crystal structure having strong c-axis orientation perpendicular to the substrate plane. A BaFe$_2$O$_4$ peak appears near 2θ-27 degrees signaling the presence of a secondary phase. Evidence of the existence of this phase is eliminated after the annealing procedure.
Fig. 25. X-ray diffraction pattern for Ba-hexaferrite (M-type) film. All significant diffraction features are referenced to (0, 0, 2n) indices having space group P6/mmc. The single BaFe$_2$O$_4$ peak appearing near 2$\theta$~27$^\circ$ disappeared after a post-deposition anneal procedure (see inset). (* denotes SiC substrate peaks.)

The FMR linewidth was significantly reduced by the post-deposition heat treatment. The as-deposited films’ FMR linewidths of ~220 Oe was reduced to ~100 Oe after the post-deposition annealing (see Fig. 26), with a measurement of 96 Oe after the optimal two-step annealing process. A $\Delta H$ value of 96 Oe compares well with values reported for BaM films grown on lattice matched non-semiconducting substrates$^{126,127}$. The improvement of the magnetic properties of films after annealing indicates assorted defects within the film have been eliminated by the annealing process. XPS does not show evidence of silicon diffusion at the surface of the annealed films.
Fig. 26. Reflected power derivative as a function of applied magnetic field in the region near the ferromagnetic resonance at 53 GHz. The linewidth measured as the peak-to-peak power derivative is 96 Oe for the post annealed BaM film deposited on 10 nm MgO (111)||SiC (0001).

4.3.4. Thick and large BaM/SiC film for the device applications

The best GEN-III films have an FMR derivative power peak-to-peak linewidth of 96 Oe, which represents high enough quality for microwave device applications. However, most BaM devices require the film thickness from 2 µm-100 µm depending on the application. To meet this goal, we explored thick film deposition based on the GEN-III techniques.
In heteroepitaxial growth, at a critical thickness depending on the film/substrate interface and film quality, cracks will form during cooling. This is due to the large elastic energy introduced by the thermal expansion mismatch. In other words, cracks form to relieve the large cumulative mismatch strain. In our experiments, as expected, BaM film grown on SiC by PLD showed cracks when the thickness exceeded 13 µm. Therefore, LPE is the only approach to grow high quality epitaxy films thicker than 13 µm. We also noticed that the cracks tend to form at these misorientated grain boundaries, dislocations, and defects, which was revealed in Fig. 27.

Fig. 27. SEM images of (a) cracked BaM film grown on SiC substrate, (b) expanded view of the circled region in (a), and (c) expanded view of the circled region in (b).
The as-deposited films, having 2 µm-13 µm thicknesses, were measured to have 200-300 Oe FMR linewidths. In preparation for device fabrication, high quality BaM films (2-5 µm) grown on 2 inch sapphire wafer, were obtained based on optimized processing conditions. These films served as the host materials for the magnetic planar micro-inductor fabrication.

4.4. Discussion

In this section, we discuss in length the impact of the interface on the microwave loss and time resolved film quality, which are two critical factors for the successful microwave application.

4.4.1. The effects of interface diffusion upon the film microwave loss

First, the properties of all three generation films are summarized in Table 2.

<table>
<thead>
<tr>
<th>Film Generation</th>
<th>Film Structure</th>
<th>$4\pi M_s$ (KG) +/-0.3</th>
<th>Easy/ Hard $H_c$(Oe)</th>
<th>FMR $\Delta H$ (Oe)</th>
<th>C-axis Orientation Dispersion</th>
<th>Interface Diffusion Range ($\mu$m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GEN-I PLD</td>
<td>BaM//SiC</td>
<td>3.8</td>
<td>1403 1228</td>
<td>2000</td>
<td>Medium</td>
<td>0.25</td>
</tr>
<tr>
<td>GEN-II PLD</td>
<td>BaM/ Buffer/SiC</td>
<td>4.1</td>
<td>1000 389</td>
<td>500</td>
<td>low</td>
<td>0.10</td>
</tr>
<tr>
<td>GEN-III PLD/MBE</td>
<td>BaM/MgO/ SiC</td>
<td>4.1</td>
<td>855 160</td>
<td>96</td>
<td>Lowest</td>
<td>0.085</td>
</tr>
</tbody>
</table>
Table 2. The properties of three generations of BaM/SiC films, including layer structure, saturation magnetization, coercivity, FMR linewidth, and crystal structure. The buffer layer represents the \([\text{MgO(A)/BaM(B)}]_n\) interwoven buffer layer where A and B represent number of laser shots and n represents cycle.

From Table 2, we clearly see that reduction in interface diffusion correlates with improved magnetic and microwave properties, and better crystal structure quality. The interface diffusion can be illustrated by depth profiles, which are shown in Fig. 28, Fig. 29, and Fig. 30, for samples of three generations, respectively. In Fig. 28, we clearly see in GEN-I samples, without any buffer layer between BaM and SiC, Si diffused substantially into the film interface. The diffusion range was estimated at \(\sim 0.25\ \mu\text{m}\). From Fig. 29, a sharper interface is observed with \(0.1\mu\text{m}\) in GEN-II sample, which applied the interwoven BaM/MgO buffer layer. In Fig. 30, there is an even sharper interface, less than \(0.1\mu\text{m}\), compared with GEN-II sample.

![Graph](image_url)

**Fig. 28.** Depth profile of GEN-I sample.
Film defects, porosity, grain boundary and misorientation of grains in the film are all responsible for broadening FMR linewidth. In addition, the diffusion region has a non-uniform magnetization distribution, therefore has a contribution to FMR linewidth as well. To evaluate this effect, let us first review the FMR theory.

\[ \frac{\omega}{\gamma} = H_0 + \frac{2A}{M} k^2 \]  \hspace{1cm} (1)
We may arrange equation (1) as

\[
\left( \frac{\omega}{\gamma} - H_0 + \frac{2A}{M} \frac{\partial^2}{\partial z^2} \right) m = 0 \quad (2).
\]

The exchange field is defined as

\[
\tilde{H}_{\text{exc}} = \frac{2A}{M} \nabla^2 M = \frac{2A}{M^2} \frac{\partial^2}{\partial z^2} (M_0 \tilde{\alpha} + \tilde{m}).
\]

This means that the internal static field is re-defined as follows in a non-uniform \( M_0 \)

\[
H'_0 = H_0 + \frac{2A}{M^2} \frac{\partial^2}{\partial z^2} M_0 \quad (3)
\]

As known

\[
\Delta H = \frac{\Delta \omega}{\gamma} = 2\alpha H
\]

For simplicity, we here assume \( \alpha \) is constant. Any variant \( \frac{\partial^2 M}{\partial z^2} \) will increase the FMR linewidth up to \( 4\alpha A \frac{\partial^2}{M^2} \frac{\partial^2}{\partial z^2} M_0 \), which was illustrated in Fig.31.
From this point, sharp interfaces are desirable to minimize the variation of $M_0$ in the film and to reduce the FMR linewidth, correspondingly. In the experiments, our approach is to introduce an effective buffer layer to minimize the diffusion in high temperature regime and reactive environment. The key to the successful growth of GEN-III films was to grow an MgO film to a minimum thickness of 80 nm. The dependence on the thickness could be explained by the complete film formation at a certain number of monolayers. This number depends on the substrate and film physical-chemical properties and also the growth techniques. For the growth condition
we used, we speculate that the MgO layer forms continuous completely at 63 nm (15 monolayers), and additional 17nm (5layers) of continuous film will effectively cut off all possible low energy channels (dislocations) within the first 15 layers. From this perspective, the completion of the MgO film to 80 nm could be considered and served as an effective buffer layer to prevent interface diffusion in later high temperature and promote epitaxy growth BaM.

4.4.2. The effects of aging upon the magnetic properties

For practical applications, the film's physical and mechanical stability over time is essential. In order to evaluate the BaM film quality as a function of room temperature aging, we returned to the original samples grown more than 18 months ago. There, we observed changes in their structural and magnetic properties that were unexpected and in some cases remarkable. Films studied here include those grown on bare SiC (i.e., GEN-I) as well as some with MgO interwoven buffer layers (i.e., GEN-II).

The film aging effect was first noticed by collecting hysteresis loops by vibrating sample magnetometry of older films. In Fig.32 (a), we illustrate the as-grown hysteresis loops of the GEN-I film grown under 300 mTorr oxygen pressure. These data represent a benchmark for changes observed in the older films designated GEN-I-Wet and GEN-I-Dry. In these data, one sees a uniaxial anisotropy with the magnetic easy axis aligned out of the film plane. The anisotropy field is difficult to ascertain since the hard axis loop does not saturate, but we estimate the $H_a$ to be 13.5-14.5 kOe. These values are significantly less than single crystal BaM values typically quoted at 17 kOe. The reason
for this discrepancy we believe is the diffusion of Si into the film and its cation substitution. Fig. 33(a) is an SEM micrograph of the BaM film morphology in the as-grown state. One sees hexagonal grains of approximately 0.3-0.5 µm in diameter arranged with their basal planes parallel to the film plane. Figure 33(d) is a similar micrograph taken of a film (i.e., GEN-II) grown at lower pressures and higher temperature with an MgO interwoven buffer layer. Clearly, this film is of a superior quality in which larger hexagonal grains (1.5-2 µm in diameter) are similarly oriented in fig 33 (b) with their basal planes parallel to the film plane.

Fig. 32(b), similar hysteresis data are shown from the GEN-I-Wet film collected after 18 months of room temperature aging in a desiccator. Clearly, the hysteresis loop shape has dramatically changed. A significant increase is seen in the coercivity from 1600 Oe to 5000 Oe, and the preference for out of plane anisotropy is reduced to nearly an isotropic state. Surprisingly, the saturation magnetization remains largely unchanged near 4000 G. Figure 33b is an SEM micrograph of this film's microstructure. The hexagonal platelets seen in Fig. 33a have been replaced with a herringbone arrangement of acicular particles in which the long axis is of the same magnitude as the platelets of figure 2a with the short axis about 0.13 µm. It may be that these particles are in fact the hexagonal platelets now arranged with the basal plane orthogonal to the film plane.

In Fig. 32(c), hysteresis data are presented for the GEN-I-Dry sample. In this case, the SiC substrate was wet -etched followed by a dry plasma etch and hydrogen termination. The hysteresis loops bare resemblance to the original film data collected 18 months ago in that the saturation magnetization remains near 4000 G, where as the coercive fields have increased from 1600 to 1750 Oe. However, what is remarkable is that we now observe a
uniaxial anisotropy with the magnetic easy axis aligned in the film plane. This in fact is opposite to that of the original film.

Fig. 32. The hysteresis loops of (a) the generation I sample prepared at 300 mTorr, which represents the VSM measurement of sample GEN-I-Wet and GEN-I-Dry as grown. (b) the sample GEN-I-Wet recently measured after the samples aged 18 months. (c) the sample GEN-I-Dry recently measured after the samples aged 18 months.

The GEN-I-Dry film morphology is depicted in Fig. 33c. Comparing this
morphology to that of Fig. 33a, we see an increase in acicular particle size to 1.5 \( \mu \text{m} \) (long axis) and 0.3-0.5 \( \mu \text{m} \) (short axis). The grain size dispersion appears to be broad and perhaps bimodal. Once again the morphology and magnetization data are consistent with hexagonal platelets arranged with their basal planes orthogonal to the film plane.

X-ray diffraction data as \( \theta-2\theta \) scans using Cu K\( \alpha \) radiation are presented in figures 34a, 34b, and 34c. In Fig. 34a, the XRD pattern is for the as-grown sample in which all diffraction peaks are indexed to the BaM hexaferrite phase. The profile is dominated by (0, 0, 2n) diffraction peaks verifying the strong crystal texture present in the film. Figure 34b are corresponding data for the GEN-I-Wet film sample. In these data, all peaks are indexed to both the M type and a secondary W type (BaFe\(_{18}O_{27}\)) hexaferrite phase. The appearance of the W-type ferrite phase (as weak peaks) is surprising since no previous reports have alluded to the time evolution of M type to W type hexaferrite. This trend towards the transformation of M type to W type hexaferrite is more pronounced in figure 34c (GEN-I-Dry) where the W ferrite peaks are dominant.

In review of these data and trends, it is unclear as to the dominant mechanism that gives rise to these dramatic changes in the magnetic, structural, and morphological properties of these films. It is likely that the strain existing at the film-substrate interface is the driving force behind these changes. If the strain energy is sufficiently large to overcome the activation energy of diffusion one can expect the diffusion of Si into the hexaferrite. Si was speculated to cause the transformation from M type to W type ferrite\(^{129}\). The substrate preparation conditions also play an important role in this transformation. From the evidence provided it appears that the transformation is more complete in those films prepared using a dry etched SiC. This may be due to the fact that under optimized dry
etching caused severe substrate surface damage prior to the film growth. It is encouraging that samples studied in which buffer layers were used at the film-substrate interface do not show signs of degradation, diffusion, or, structural and magnetic changes.

Fig. 33. The SEM images of (a) the GEN-I sample prepared at 300 mTorr, which is representative for the sample GEN-I-Wet and GEN-I-Dry as grown, (b) the sample GEN-I-Wet recently scanned, (c) the sample GEN-I-Dry recently scanned and (d) the sample G2 as grown.
Fig. 34. The XRD spectrum of (a) the GEN-I sample prepared at 300mTorr which represented sample GEN-I-Wet and GEN-I-Dry as grown, (b) the sample GEN-I-Wet recently collected. (c) the sample GEN-I-Dry recently collected. ‘W’ in the peaks index represents the W-type BaFe$_{18}$O$_{27}$.
Chapter 5. MIC Fabrication

As first stated in Chapter 1, the goals of this research program is to lay the foundation for the integration of ferrite-based passive microwave devices with semiconductor-based active device platforms. As such, one such goal is to explore the integration of BaM ferrite films on SiC substrate in device level. To date, most ferrite devices are fabricated in bulk form, such as an X-band T/R module (see Fig. 35) used in land based missile or air fighter jet phase array radar.

![Fig. 35. T/R modules and its applications](image)
This module has the dimension of 64.5mm in length, 13.5mm in width and 4.5mm height. Each phased array has thousands of T/R module elements and each element costs more than $1000. Is it possible to make the module smaller in size and better in performance? As seen, T/R modules include passive devices such as circulators, isolators, phase shifters, delay lines and MMICs such as low noise amplifiers (LNA), high power amplifiers (HPA); and CMOS devices and heat sinks for HPA. These passive devices are usually fabricated on insulating oxides substrates, while MMICs use GaAs and CMOS employ Si substrates. For heat sink, copper or other metal are usually adopted. As we discussed in the previous chapters, SiC has gained much attention in the semiconductor community as a next generation material for GaAs and Si devices. Meanwhile, SiC can also handle much higher power than GaAs, which could eliminate the need for heat sinker in the module. Furthermore, SiC has better thermal conductivity than copper, which could enhance the power capability at the system level. Noticeably, well established SiC processing follows most existed semiconductor processing techniques. Provided that these passive devices could be fabricated on SiC substrates, then all these components could be integrated onto a single SiC substrate without sacrifice to performance, in other words, a T/R MIC.

5.1. Self biased circulator fabrication on SiC substrate

Given as the most important, versatile and widely used microwave device, we have focused much of our research upon addressing the fabrication and production needs
of what we envision as next generation circulator devices on semiconductor systems platforms. Specifically, we have adopted SiC as the host platform, since it is widely accepted as a possible next generation microwave electronics substrate.

A typical use of the circulator is in telecommunication (radar, mobile phone) equipment where it enables simultaneous sending and receiving of electromagnetic signals. This is illustrated in Fig. 36.

Fig. 36. (a) Components of a stripline Y-junction circulator. Permanent magnets provide the magnetic field necessary to bias the ferrite loaded junction. (b) Magnitude of the electric field in the stripline Y-junction circulator calculated by finite element methods. Low insertion loss in the forward direction of propagation (port I – port II) and high isolation in the reverse direction (port I – port III) are observed. (c) Simplified block diagram of a T/R module. Switches and a circulator are utilized to guide the high power transmitted signal to the antenna in the transmit mode and to guide the low power signal from the antenna to the low noise amplifier and the receiver in the receive mode. The circulator also serves to protect the high power amplifier by dissipating the power reflected from the radiating antenna in the load.
The successful integration relies on two key technological advances: (i) the successful growth of oriented, high quality magnetic oxide films on semiconductor substrates, and (ii) the effective patterning of magnetic oxide films into device and integrated circuit structures. The processing (growth and patterning) of semiconductor film structures has been established for many years, while processing of magnetic oxide film structures remains a significant challenge. We have demonstrated in previous chapters the growth by pulsed laser deposited c-axis oriented, quasi-single crystal, BaM (films on wide band-gap semiconductor substrates, SiC$^{134}$ and GaN$^{135}$. In addition, we have successfully grown ~15 µm thick, high quality, BaM films (having ~200 Oe FMR linewidth) on SiC using the same technique. Based on these results and proven thick film growth methodologies, 100 µm films are feasible using PLD seed layers followed by liquid phase epitaxy (LPE). This approach provides a reasonable pathway to integrating thick ferrite film microwave devices with semiconductor systems. The growth of very thick BaM via LPE is identified as future work.

In conventional circulator designs, two bulky permanent magnets (see Fig. (a) ) are required to bias the ferrite to enable the circulation. Because of the bias magnets, conventional circulators are three dimensional constructs that limit attempts at planar integration. To realize self-biased, planar circulators and other microwave passive devices, we propose to overcome the films demagnetizing field by introducing other shape anisotropies. Specifically, we propose the patterning of BaM films into arrays of cylindrical pillars. The demagnetizing field of the pillar will realign the spontaneous magnetization along the long axis of the pillar or column and hence perpendicular to the film plane. For a thin film the demagnetizing field is significant, $H_D \sim 4\pi M_s = 4000G$. 

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For an array of cylindrical shaped samples, the demagnetizing field will be reduced considerably. For example, the etched film has aspect rations of 1 to 5, which reduces $H_d$ to 75% of $4\pi M_s$ ($\sim 3000$G) along the easy axis. Furthermore, a pillar array may also be used as a seed layer in the growth of thicker films by liquid phase epitaxy. This approach to thick film processing was shown effective by Yoon et al. Assuming an aspect ratio of 40 to 1, see Fig. 37, was grown by this approach, less than 0.7% $4\pi M_s$ ($\sim 30$G) can be realized along the easy axis, this could be treated as a self-biased film for applications in planar circulator fabrication.

![Fig. 37. A cartoon illustration of PLE grown on BaM pillar arrays.](image)

However, the patterning of near- and sub-micron features in BaM remains a key challenge that we address presently. In the following section, we focus on high-rate reactive ion etching of c-axis oriented quasi-single crystal barium hexaferrite films, deposited on 6-H silicon carbide (0001) substrates.
5.2. BaM film structure patterning technique

It is widely acknowledged that the depth control afforded by wet-etching of ferrites is a key limitation to the etching of ferrite materials. Attempts at dry etching ferrite materials using Ar ions and laser thermal etching resulted in severe lateral over-etching and excessive film damage, respectively. Furthermore, isotropic etching processes cannot reliably provide sub-micron lateral features; clearly, an anisotropic dry etch process is in critical need.

Dry etching experiments were performed in an ICP-98A system at the Institute of Microelectronics, Chinese Academy of Sciences (Beijing, China). The system had two independent radio frequency sources, one inductive and one capacitive, operating at the same frequency, 13.56 MHz. These two sources were used to generate high-density plasma and to introduce a self-biased electrical field, respectively. Before etching, optical lithography was performed to transfer the photomask test pattern to the photoresist (Shipley Model AZ5214-E). The depths of the pillars were measured after the dry etching process using a Veeco DekTak surface profilometer. The estimated error in the depth profiling step was ~10 nm, which was considered in the estimated etch rate uncertainty. The etched profiles and lateral cross sections were examined by scanning electron microscopy (SEM).

In the RIE/ICP process, three important parameters were optimized: the process gas mixture, the chamber pressure, and the capacitive electrode RF power (with/without ICP inductive RF power). In this experiment, the plasma chamber was pumped by a 500 lt/s turbo-molecular pump (TMP), maintaining a dynamic vacuum pressure of ~10⁻⁶ Torr.
The working gas pressure was varied by adjusting the gas flow rate in concert with the conductance of the TMP. A dynamic gas flow rate of 240 sccm was maintained throughout the procedures. During the film etching, the flow rates of each gas were controlled via mass flow controllers. The sample holder was water-cooled to maintain a fixed sample temperature of ~27°C to minimize thermally-induced damage to the film sample. The initial gas mixture, CHF$_3$/Ar, was similar to that used in conventional SiO$_2$ etching. In using this gas mixture (as well as CHF$_3$ alone), only slight etching was experienced with little removal of film mass. The BaM film was successfully etched and patterned only after the CHF$_3$ was mixed with SF$_6$. The optimal ratio of CHF$_3$:SF$_6$, 1:3, was achieved through systematic variation of gas mixtures and repeated evaluation of etched patterns. The dependency of the etch rate to gas mixture is illustrated in Fig. 1(a).

During these measurements, the electrode RF power was maintained at 160 W. This indicates that the presence of SF$_6$ is critical and acts as the primary reactive gas. We postulate that the SF$_6$ gas produces most of the ions and erosive neutrals, which are dissociated in the plasma environment, to form atomic fluorine. Atomic fluorine chemically reacts with the BaM material to form volatile BaF$_x$ and FeF$_x$ gas complexes that are exhausted by the vacuum system. However, when only SF$_6$ gas is used, the etch rate remains substantially lower than that of the gas mixtures. This indicates that the CHF$_3$ is not only a buffer gas, which maintains plasma stability, but also provides additional energetic ions that enhance the ionization of the SF$_6$ molecules.

At an optimized 1:3 CHF$_3$/SF$_6$ mixture, the electrode RF power was varied to study its impact on the etching profile. For each trial, etching was performed for 5 minutes and the etch rate per minute as a function of the electrode RF power was determined (Fig. 38
From these data, the etching threshold power was determined to be 60 W, with a maximum etching rate of 87 nm/min, corresponding to ~240 W of RF power.

Fig. 38. The etch rates of BaM films as a function of gas mixtures (a) and RF power (b). The data in panel (a) were collected using an RF power of 160 W.

Fig. 39 (a, b and c) are SEM images of the top view (a), side view (b), and expanded side view of the optimized etched pillar array and individual elements. The images reveal a clear array of periodic cylindrical elements. The expanded view depicted in Fig. 39 (c) reveals each element in the array depicted in Fig. 39 (a and b) consists cylinders of BaM capped with photoresist. A thin PtPd metal film coats the elements to allow for enhanced imaging. The BaM cylinders appear to have vertical walls. Fig. 40(a and b) are SEM images of BaM patterned revealing a minimum lateral feature of 43 nm.
Fig. 39. (a) Top-view SEM image of the patterned BaM film array consisting of an array of 0.5-1 µm diameter pillars at a 2µm center-to-center spacing. Sample was processed using the optimal gas mixture and RF power. (b) Side-view SEM image of the same sample. (c) An expanded view of one pillar in panel (b). The individual pillar consists of a BaM cylinder with a photoresist cap on the surface. The "frost" on the element is a thin AuPd coating used to reduce fluorescence during SEM imaging.

Fig. 40. (a) Top view SEM image of test pattern designed to evaluate minimum lateral features. (b) An expanded view of the minimal lateral feature of 43 nm (at the necked region).

An important consideration of the etching procedure is its impact upon the film's magnetic properties. Since damage to the BaM film is anticipated, it is unclear if the films will be suitable for magnetoelectronics applications after etching. In Table 3, we present the demagnetizing field ($H_d$), the coercive fields (collected with the applied field aligned along both the easy, $H_{c^e}$, and hard, $H_{c^h}$, directions), and the theoretical and
experimental demagnetizing factors, $N_t$ and $N_c$, respectively. These properties are presented for the as-deposited film, after etching, and after a heat treatment at 1050°C in air for a period of 25 minutes. Values were determined by examination of the room temperature hysteresis loops collected with the applied magnetic field aligned along the in-plane (hard) and perpendicular to the plane (easy), directions. As discussed earlier, one goal of etching pillar arrays in the BaM films was to reduce the demagnetizing field ($H_d$) leading to a potential self-biased state. Alternatively, the coercive fields are important parameters in that they are acutely sensitive to defects and structural imperfections and reflect the static magnetic losses in the film/pillar arrays.

As seen in Table 3, etching the pillar array significantly reduced the demagnetizing field of the as-deposited film; a reduction of 19.3%. As anticipated, the etching procedures raised the coercivity (25%) from the as-deposited state. This was no doubt due to damage introduced to the film from plasma-film interaction which resulted in the effective pinning of magnetic domain walls as they were swept through the film during the collection of the hysteresis loop. The post-etching heat treatment proved remarkably effective in healing those defects, resulting in a 52.8% decrease in $H_c^e$. These improvements were mirrored in values of $H_c^h$ (reduction of 79.4%). Examining the demagnetizing factor, one sees that the theoretical values are well-matched by experiment.
<table>
<thead>
<tr>
<th></th>
<th>$H_d$ (%Δ) Oe</th>
<th>$H_c^v$ (%Δ) Oe</th>
<th>$H_c^h$ (%Δ) Oe</th>
<th>$N_t$ (%Δ)</th>
<th>$N_e$ (%Δ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited Film</td>
<td>3886</td>
<td>1600</td>
<td>189</td>
<td>0.99</td>
<td>0.97</td>
</tr>
<tr>
<td>Etched film</td>
<td>3137 (-19.3%)</td>
<td>2000 (+25%)</td>
<td>332 (+75.7%)</td>
<td>0.75</td>
<td>0.78</td>
</tr>
<tr>
<td>Etched film after anneal</td>
<td>3100 (-20.3%)</td>
<td>756 (-52.8%)</td>
<td>39 (-79.4%)</td>
<td>0.75</td>
<td>0.77</td>
</tr>
</tbody>
</table>

Table 3 Demagnetizing fields ($H_d$), coercive fields ($H_c$), and demagnetizing factors ($N$) of BaM films before and after etching and after heat treatment. Note: %Δ represents percent change from as-deposited condition. $N_t$ was calculated approximately using oblate ellipsoid model$^{141}$, where $m$ represents aspect ratio of pillar.

$$N_t = \left( \frac{m^2}{m^2 - 1} \right) \left[ 1 - \frac{1}{(m^2 - 1)^{1/2}} \arcsin \left( \frac{(m^2 - 1)^{1/2}}{m} \right) \right].$$

In summary, the introduction of sulfur hexafluoride to methyl trifluoride was found effective for the successful reactive ion etching of M-type barium hexaferrite. The presence of CHF$_3$ was shown to be critical to both the etching rate and the quality of vertical sidewall profiles. The optimum gas mixture was a ratio of one part CHF$_3$ to three parts SF$_6$, with an electrode RF power of 240 W. These conditions lead to the maximum etch rate of 87 nm/min and the patterning of nanoscale features of less than 50 nm in films as thick as 2 µm. The magnetic properties, especially those reflecting magnetic loss, where shown to degrade with etching. However, post-etching heat treatments showed that the magnetic properties were recovered and even improved relative to their virgin state. The effective etching of magnetic oxides, and specifically microwave ferrites, is an essential advancement that enables fabrication of planar microwave passive devices and their ultimate integration with semiconductor integrated circuit platforms.
Chapter 6. Summary of research results and recommended future work

In the previous chapters, we have demonstrated two essential BaM processing techniques necessary for the eventual integration of ferrite-based microwave passive electronics with semiconductor-based active electronics: first, the development of epitaxial ferrite thin film deposition via PLD on wide band gap semiconductor substrates, SiC, second, the development of pattern transferring for BaM films using a reactive dry etching technique. Here we provide a summary of research accomplishments and identify future work to further pursue these ultimate goals.

6.1. Summary

The growth of epitaxial BaM on wide bandgap semiconductor substrates has proven challenging. The incompatibility of the substrate-and–film and quick formation of a native surface oxide on SiC substrate at high temperature and oxygen pressure were major problems. Therefore, efforts were focused on manipulating starting surface conditions in order to overcome these obstacles and provide a suitable surface for the growth of high quality, low loss, BaM. As the research advanced, different strategies were explored; these are separated into three stages.

In the first stage, i.e. generation I, surface preparation techniques were explored, including both wet chemical and dry etch procedures. The wet chemical etch preparation sharing standard semiconductor cleaning processes were employed including the
exposure to boiling $\text{H}_2\text{SO}_4 + \text{H}_2\text{O}_2$, HF + $\text{H}_2\text{O}_2$, HCl+$\text{H}_2\text{O}_2$ and rinsing with demonized water. The dry etch process was carried out using ion beam bombardment with Ar gas in a Kaufman-type ion source operating between 500-1000 eV and followed by hydrogen gas treatment to hydrogen terminate the surface. Both procedures were proven effective and sufficient for substrate surface treatment prior to deposition by showing a significant impact on the quality of the resulting Ba-hexaferrite films. Due to the compatibility with CMOS platform, wet preparation was adopted throughout the project. In meanwhile, PLD processing conditions were optimized at substrate temperatures of 910°C, oxygen pressure of 20 mTorr, and laser energy of 280 mJ/shot. Although, the resulting films were characterized of epitaxial growth of c-axis textured, these films suffered the moderate DC and AC magnetization properties. To further improve the film quality, judged by magnetization properties, we focused on the interface manipulation, more specifically, in order to minimize defects, porosities, grain boundaries and misorientation of grains in the film.

Our first attempt was to introduce a pure MgO buffer layer deposited by PLD. However, we found the films had poor uniaxial magnetic anisotropy, which was explained by the quick oxidization of SiC during the PLD ablation (5minutes) in a high temperature (910°C) oxygen environment. We adopted the practice of using a thin graduated MgO multilayer in the early stages of film growth. The multilayer structure consisted of MgO layers interwoven with BaM layers, shown in Fig. 19, chapter 5. Films grown with this graduated buffer layer demonstrated superior uniaxial magnetic properties to those without this modification. In this stage, i.e. Generation II, we optimized the laser frequency condition during deposition, in order to enhance adhesion
and epitaxy at the interface. Laser repetition rate was slowly raised from 2 Hz to 16 Hz for the first 5 minutes, and then fixed at 16 Hz for the remaining 30 minutes of growth. As a result, the ferromagnetic resonance linewidths of these samples were reduced to 500 Oe from 1200 Oe. However, post-deposition heat treatments were found largely ineffective in further reducing the FMR linewidth from 500 Oe. This led us to focus on processing schemes intended to further mediate the strain and diffusion across the film-substrate interface.

Since, MgO (111) epitaxy films could be deposited at ~150 °C on 6H-SiC by MBE\textsuperscript{142}, and theoretically, the MgO buffer layer ideal to reduce the lattice mismatch between the BaM and the SiC from 4.76\% to 1.33\%. We chose to prepare the MgO (111) layer on SiC substrates using MBE as a technique to improve the interface layer. As a result, BaM films having \(4\pi M_s\) of 4.4 kG and \(\Delta H\) of 220 Oe were successfully grown by pulsed laser deposition on single crystal 6H silicon carbide substrates buffered with a 10 nm crystalline MBE-grown MgO (111) layer. These films are characterized as having basal planes parallel to the substrate plane. After annealing, the best films had an FMR derivative power linewidth of 96 Oe, which is of sufficient quality to pursue microwave device applications. To meet the thickness requirements for typical microwave device applications, 2\(\mu\)m-13\(\mu\)m thick films was successfully grown on SiC substrates with 200-300 Oe FMR linewidths in the as-deposited condition. In preparation for device fabrication, high quality BaM films (2-5\(\mu\)m) grown on 2 inch sapphire wafer, were obtained based on the optimized processing conditions. These films served also as the host materials for the magnetic planar micro-inductor fabrication.
In addition, the film's physical and mechanical stability over time was evaluated as a function of room temperature aging. Films studied include those grown on bare SiC (i.e., GEN-I) as well as some with MgO interwoven buffer layers (i.e., GEN-II), which are all more than 18 months ago. Although, we observed GEN-I samples experienced unexpected, in some cases remarkable, changes in their structural and magnetic properties. We found GII-samples, in which buffer layers were used at the film-substrate interface, show little signs of degradation, diffusion, or, structural and magnetic changes. This is an encouraging property for real device applications.

In the end, to demonstrate the feasibility of microwave passive devices fabrication and their integration with semiconductor integrated circuit platforms, an effective etching of BaM films was developed. The high-rate reactive ion etching of c-axis oriented quasi-single crystal barium hexaferrite films, deposited on 6-H silicon carbide (0001) substrates, has been demonstrated. Arrays of BaM columns, having diameters of 1-2 µm and sharp vertical walls, were etched from BaM films at rates as high as 87 nm/min using an optimized sulfur hexafluoride and methyl trifluoride (SF$_6$:CHF$_3$ 3:1) gas mixture. Lateral features as small as 43 nm were also fabricated.

This advancement enables potential magnetic microwave device and possible fabrication of magnetic quantum devices consisting of ferrite films on SiC substrate.

**6.2. Recommended future work**

Despite the above achievements, there are still many challenges for the realization of MICs. The most significant ones are discussed below.
The ultimate goal of film growth, especially for crystal ferrite films on semiconductor platforms, is to develop viable techniques leading to significant growth temperature reduction without deterioration of film properties. PLD is a proven technique for high quality films growth in high temperature and highly reactive environment. What has been less thoroughly explored is its ability to grow films at low temperatures. As discussed in Chapter 2, pulsed laser ablation provides much higher supersaturation than other conventional vapor deposition techniques. This may lead to the epitaxial growth of ferrite films at low temperature.

The ferrite film devices typically require film thicknesses in the range of 2 µm to 100 µm. Therefore, an etching rate of ~1 µm/min is desirable. Based on our RIE etching rate of 87 nm/min, etching rates on the order of ~1 µm/min could be achieved by combining RIE with ICP, where the addition of ICP would tremendously increase the ion density in the plasma.

At the device fabrication level, a conducting ground layer has to be incorporated. One possible way is to deposit platinum on SiC followed by BaM growth on a platinum film. Platinum was successfully used as a buffer layer in the growth of BaM and is stable during high temperature processing.
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