A review of iron nitride based thin films development

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Abstract. Thin film technology has taken a lot of area in the industry due to their properties which is better than their parents bulk materials. One of the interesting thin films that has yet to be fully explored is iron nitride based thin films has been attracting attention for the past few years especially in the semiconductor technology. Crystal structure and magnetic properties on the film which depend greatly on the growth method, deposition technique, gas flow, pressure and many more. Suitable parameters allow the presence of required iron nitride based thin films stoichiometry. In semiconductor application, magnetization properties play an important role of developing iron nitride thin films. This will give rise to the formation of strong magnetic moment thus increasing the corrosion resistance of the thin film. However, the difficulties of growing a pure phase of these iron nitrides thin films makes it more interesting to study and recent researches have shown findings that open the possibilities in enhancing properties of this iron nitride based thin films.

1 Introduction

Research interests on the binary nitrides thin films has grown rapidly due to their excellent properties in many areas including semiconductor and micromechanical. However, the commercialization of these type of nitrides is hampered by several challenges, including the instability of the formation and high cost due to the process used to synthesis these nitride is rather a difficult routes and require a system like Electron Beam Physical Vapor Deposition (EB-PVD) or Molecular Beam Epitaxy (MBE) techniques and many more. Recently, transition metal nitrides (TMN) have attracts researches because they are highly electrically conductive, thermally stable and have high melting points and exceptional hardness and corrosion resistance[1]. The use of TMN as coatings has also been successfully explored due to properties like high hardness, biocompatibility and there are recent effort to tailor lattice constant and electrical mechanical and optical properties of this nitrides[2].

TMN is often linked to development of binary thin films. This is because compared to bulk samples, thin films possess better physical and mechanical properties. Thin films is a thin layer material applied to a surface of substrate to be coated or to a previously coating to form layers. The growth of thin films is firmly affected by the substrate which results in the formation of microstructure and determining film properties. One of the interesting traits of thin films is they are usually crystallographically oriented in a specific way (depending on the growth of the thin films) with respect to the underlying substrate which is known as epitaxial thin films. Few binary nitrides have taken an interests in many aspects of technology are boron nitride (BN) and gallium nitrides which is vastly used in the development of UV light applications

Boron nitrides thin films for instance, crystallizes in two forms; a cubic zinc blende and a hexagonal structure. It was found that different crystal structure gives different role in the electronic semiconductor applications. Some of the important applications of boron nitride thin films is as diffusion source. This method can be used to fabricate planar diodes only one photomask by diffusing boron nitrides on the silicon dioxide windows. This will result in the ohmic contact between and nickel can be deposited directly by electroless plating on bare silicon.

Interestingly, the development of iron nitride thin films is fundamentally connected to field of basic research based on phase diagrams. Based on the different properties iron nitride thin films can possess, in this paper we are exploring the new possibilities of enhancing better quality of iron nitride thin film in many areas including semiconductor and micromechanical.

1.1 Iron nitride thin films

Iron nitrides consists of many phases with different crystal structures which results to different properties of each type of iron nitrides. Formation of iron nitrides are normally conducted by the nitriding process which results in phases such as FeN, ζ-Fe2N, ε-Fe3N and γ'-Fe4N. A study conducted by Tesseir et al[3], found that with the formation of different...
phases of iron nitrides results in higher wear resistance properties which is usually used in hard coatings application. This is due to the fact that when this binary nitrides are subjected to high temperature, the phase stability improves thus enhancing their properties. One of difficulties of growing nitrides is instability of nitrogen when incorporated with metals (especially transition metals). Therefore, nitrogen percentage needs to be determined in order to obtain preferred stoichiometry of iron nitrides. Concentrations of nitrogen given to iron nitrides will exhibit a ferromagnetic, paramagnetic and non-magnetic characteristics of the material.

During the last decades, iron nitride compounds have been intensively investigated because iron and nitrogen are among the most abundant elements in nature, but also because these compounds are very interesting from a fundamental point of view and industrial applications [4]. Iron nitrides consists of many phases with different crystal structures which results to different properties of each type of iron nitrides. Formation of iron nitrides are normally conducted by the nitriding process which has made this nitrides received attention for many years and has been widely studied due to their ability to improve many things such as surface hardness and wear resistance[5].

The work on the iron nitrides not only limited on bulk samples, extensive research has been conducted on developing iron nitride based thin film in a 3D and 2D. Due to their capability of becoming between ferromagnetic to paramagnetic, iron nitrides thin films is applicable to be used in the semiconductor area especial as magnetic storage data. The crystallographic phase of iron nitrides affected their magnetic properties. Therefore, the desirable to obtain as many pure phases as possible is one of the ways to improve this. Unfortunately, due to their metastable properties, it is significantly challenged to control the phase structure and hence the magnetic properties of iron nitrides.

Figure 1(a-d) shows AFM images of iron nitrides thin films where for AFM images all of the films exhibited uniform granular structure grains with diameter around 30 nm respectively. These grains aggregated together and left many peaks and valleys on the film surfaces which indicates good quality thin films. The only differences from the images are the parameter used to grow the samples[6]. The thin films undergone repeated nucleation process which resulted in a transition from columnar to globular microstructure, a denser microstructure. Furthermore, This results were also supported by a study conducted by Khan et al.,[7] where transmission electron images showed a homogeneous formation of phases and there were some parts with amorphous iron nitrides matric (Figure 2a and Figure 2b). Figure 2c shows an interface of the film and it does not show any signs of porosity which indicates that the film is densely packed columnar structure with low surface roughness. The last picture of high-resolution transmission electron microscope (HRTEM) shows a lattice spacing between each atomic coulomb around 3.78 nm and there is also a thin amorphous layer with flaccid structure identified by the iron nitride nanoparticles. According Hari et. al.,[8] amorphous inclusions in this films are featureless having no grain boundaries resulting in an expulsion of intrinsic stress and a smoother surface that indicates the structure of the thin films is strongly affected by the film thickness [9–11].

![Fig. 1. AFM images of transition between (a1-b2) columnar to (c1-d2) globular microstructure depending on the parameters given to iron nitride thin films][6]
Due to properties of iron nitride thin films, there has been vast research happening to synthesis ternary nitrides such as FeWN$_2$. The properties exhibit by iron nitrides sparks the interest among researchers on the possibilities of ternary metal nitrides to be used as epitaxial film layer together with boron nitrides and graphene’s via intercalation method. It is also believed that this ternary nitrides iron based thin films materials may exhibit interesting thermal, optoelectronic, semiconducting, magnetic and/or superconducting properties[12–15].

2 Deposition of iron nitrides based thin films

There are a number of techniques in growing thin films, specifically iron nitrides which is by physical vapor deposition (PVD) and/or chemical vapor deposition (CVD) However, in this paper, we will solely focus on the technique by PVD methods as one of the main advantages of PVD is the processes are clean and pollution free compare to CVD process. EBPVD and MBE are widely used because of these techniques produces good quality of films. In PVD, there are variety modes of activation of growth including electron beam, ion beam, laser beam, induction heating and cathodic sputtering[16–18]. Choosing the suitable deposition routes is crucial because it will reflect on thin film quality and it is the most important key for thin film application devices. Thin films have several stages during growth that will then determine the properties of the films such as microstructure, surface, interface, physical and mechanical properties. Thermal deposition or also known as vacuum deposition is the simplest method one could carry for preparing thinner thin films in micron. Two types of source which commonly used are resistive and electron beam source. The target is evaporated by heating the source thus condensing evaporated particles on the substrate. Sputtering is another well known technique which uses radiation for thin film deposition including dc diode (also known as dc sputtering), radio frequency sputtering (RF) magnetron and ion beam sputtering[16–19]. However, many researchers would use to molecular beam epitaxy (MBE) and electron beam physical vapor deposition (EBPVD) techniques. MBE is a term used to epitaxial growth of compound semiconductor films by process involving the reaction of one or more thermal molecular beams with a crystalline surface under ultra high vacuum conditions. This method is related to vacuum evaporation but offers improved control over the incident atomic or molecular fluxes so that sticking coefficient may take into account and allow rapid changing of beam species. Zuo et. al.[23], succeeded in growing epitaxial boron nitrides (BN) thin films with MBE. They have found appearance of small grains due to heat treatment and also formation of triangular shaped of h-BN domains which is supported both by Raman scattering and x-ray photoelectron spectroscopy (XPS) results This shows the growth route and also with the suitable parameters chose, a high-quality thin film is able to obtain. Due to the better growth deposition with MBE, Sugita et al.[24] and Golden et al.[10], did a study on the magnetic moment on Fe16N2 single crystal thin films and other iron nitride thin films phase by this technique which was rather difficult in growing them with other methods due to their metastable compound state.

Another method of growing iron nitrides thin films is by sputtering, which was studied by Rissanen et al.[25] and Wang et al.[5]. This technique was selected because nitrogen rich thin film can be produced by controlling their deposition parameters by taking into account the combination between argon and nitrogen gas given to the sputtering system. Furthermore, the film composition showed that there was small amount of oxygen surface contamination. Based on the XPS data (Figure 3 a dan Figure 3b), all samples exhibit almost similar nitrogen content which is an ideal
value of the phase in iron to nitrogen phase diagram. Figure 4a to Figure 4c show AFM images of iron nitride thin film grown by the sputtering technique. It can be seen that the roughness is low and it formed a solid films under the equilibrium conditions which are predicted to have self-affine surfaces and the roughness can be characterised as dynamic form.

![X-ray photoelectron spectra](image)

**Fig. 3.** X-ray photoelectron of (a) Fe 2p spectra and (b) N 1s spectra for samples with different parameter growth deposited by sputtering with different gas flow of nitrogen.

![AFM images](image)

**Fig. 4** AFM images of thin film grown with (a) 30 % (b) 50 % and (c) 60 % of gas flow of nitrogen fractions.

There are still many possibilities of ways in growing these iron nitrides thin films. The challenges part is this development of iron nitrides not only costly but also need a great effort in understanding their metastable state in order to enhance their capabilities in the thin film development.

### 3 Different phases of iron nitrides based thin films

FeN is known to be very sensitive to pressure and the nitrogen flow. Given the suitable temperature and pressure, it is possible to produce this thin film. Higher temperature given to the pre-deposition substrate will introduced $\varepsilon$ phase structure. The homogeneity of FeN thin films can be achieved by using higher temperature with half percentage of the overall gas flow. The crystal structure of FeN is cubic which makes silicon (100) as a suitable substrate to use in order to avoid lattice mismatch[26].
A study conducted by Fratczak et al. [4], showed that they were three phases of iron nitrides thin films which are easily produced they are \( \alpha' \)-Fe\(_{8}\)N\(_{5}\), \( \varepsilon \)-Fe\(_{3}\)N and \( \gamma'' \)-Fe\(_{4}\)N. These samples were grown by MBE in ultra high vacuum condition by changing the parameters from getting the purest form (\( \alpha \) phase) to epsilon (\( \varepsilon \)) phase which is mainly in a non magnetic form. It was found that \( \alpha' \)-Fe\(_{8}\)N\(_{5}\) is present in the \( \varepsilon \) phase, which is easily formed during the iron and nitrogen deposition. The iron formation as found to be on top of the sample surface which means that nitrogen was not diffusing deep enough. The sample is found experiencing transition from bcc to fcc and hexagonal crystal structure. Therefore, \( H_2 \) is added in the gas source in sputtering to lower the chemical potential on the sample surface. However, this resulted with no \( \alpha' \) phase formation. The \( \varepsilon \)-Fe\(_{3}\)N is the easiest phase to obtain while \( \gamma'' \)-Fe\(_{4}\)N was theoretically predicted. Epsilon phase iron nitride occurred during the mixture of hydrogen and nitrogen in gas flow. The combination process between nitrogen atoms into nitrogen molecules is not possible with the presence of hydrogen due to their chemical factor. The epsilon phase can be in magnetic or non magnetic depending on the nitrogen content incorporated in the compound. The \( \varepsilon \)-Fe\(_{3}\)N phase has a hexagonal close packed (hcp) crystal structure.

Temperature plays an important role in formation of iron to nitride thin film phases. For example, \( \alpha' \)-Fe\(_{8}\)N thin film occurred at temperature at 100°C since it will start to disintegrate around 180°C. It was also reported within this range of temperature, it is possible to grow other iron nitrides thin films such as \( \gamma'' \)-Fe\(_{4}\)N and \( \varepsilon \)-Fe\(_{3}\)N. There was a peak shift in XRD data of \( \alpha' \)-Fe\(_{8}\)N with higher power/voltage applied to the deposition. According to Dirba et al. [27] this behaviour indicates the elongation of the c-axis by introducing the nitrogen interstitial as observed in other sputtered Fe-N thin film. The phase formation is greatly influenced by the choice of substrate material and symmetry. Determine the suitable parameters such as nitrogen content and the voltage also play an important role in the development of iron nitride based thin films. Growing sample with higher temperature will increase possibilities of residual presence thus leading to low quality of crystalline thin films.

A much broader region is expected from iron nitride thin films phase diagram and more studies should be conducted in order to understand the iron nitrides thin films properties and characteristics.

### 4 Properties of iron nitride thin films

#### 4.1 Magnetic properties

Iron nitride is known as magnetic materials. Iron is by far is of interest because it is the cheapest magnetic element with properties like volume-sensitive, with a critical interplay between structure and magnetism. \( \alpha \) Fe phase which is in BCC crystal structure is a weak ferromagnetic while \( \gamma \)-Fe (FCC crystal structure) is particularly sensitive to lattice volume, and some conditions may find that this phase are able to range from high moment or low moment or non magnetic at all depending on lattice parameter. Uniform permeability is needed in iron nitride thin films because this will indicate the capability of the thin film to perform in extremely high density magnetic condition as well as in the integrated inductors operating in the gigahertz range. The high permeability of GHz frequency and low energy loss can be obtained by adjusting the component and phase evolution of the thin films. Ferromagnetic nature of FeN\(_4\), for instance, showed presence of magnetic fields which leads to a combination between magnetic and electric hyperfine interactions. The structure of Fe\(_4\)N consists of Fe-N and Fe-Fe bonds combine together. This bond is greatly influence by the nitrogen on the electronic structure[25–27].

Previous experiments [28–30] by numerical studies reported the lattice constant is used in the geometry optimization in order to obtain the relaxed structure of thin film. Ferromagnetism in iron nitrides is depending upon nitrogen attractions on more electrons from Fe neighbouring atoms, and these electrons are incompletely screened thus affecting the magnetic moment. The lattice constant also effects the variation of magnetic properties of iron nitride thin films. The variation of magnetic moment also might be owing to the hybridization of the interstitial N atoms with the neighbouring of Fe atoms which will disturb the deformation of the atoms in the structure.

#### 4.2 Corrosion resistance

Corrosion resistance is conducted on nano structured thin film by the EIS technique. EIS technique is a response of a circuit to an alternating current or voltage to a function of frequency. The stability of iron nitride thin films usually increased with decreasing of nitrogen flow rate. The shorter or longer time of formation of passivation layer on thin film surface will determine higher or lower corrosion resistance. Longer formation time for passivation layer indicates to the minimal grain boundary density which usually occur in thinner thin films. Low corrosion resistance usually occurs because higher heterogeneity due to the presence of more nitrogen concentration in the iron nitride film and passive film interface will in low corrosion resistance. Meanwhile, higher corrosion resistance is affected by thin film thickness and the thin film is regarded as more stable phase with higher content of metal nitrides [26, 31–32].

### 5 Conclusions

There are still many areas of iron nitrides thin films which is referred to phase diagram that is waiting to be explored. Extensive studies and research shall be conducted in order to enhance the capabilities of iron nitrides thin films not only...
in semiconductor applications but open up the possibilities to order applications such as hard coating and superconductor materials as with their atomic arrangement and crystal structure iron nitride thin films are able to withstand higher temperature and also possess of higher hardness.

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