The Study on Al$_x$Ga$_{1-x}$N Film Deposition by Radio Frequency Magnetron Sputtering

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Abstract: A series of Al$_x$Ga$_{1-x}$N films are deposited on Si (111) substrates by radio frequency magnetron sputtering with different experimental parameters. Crystallographic, elemental components and surface morphologies of films are investigated in terms of their deposition parameters. The results reveal that the films grow along with the (004) crystal direction and have a more Al component than the target, which is attributed to the higher bond energy of Al-N. A higher pressure and nitrogen concentration lead to more surface structures such as bubbles on the Al$_x$Ga$_{1-x}$N films. Using a pressure of 1.0 Pa and nitrogen concentration of 33%, Al$_x$Ga$_{1-x}$N films with good quality are finally achieved.

1. Introduction

III-V group nitride semiconductors (GaN, AlN, BN, InN) and their alloys have great application potential in electronic and optoelectronic devices. In particular, Al$_x$Ga$_{1-x}$N, which is the alloy of GaN and AlN, has become one research hot spot in recent years. Al$_x$Ga$_{1-x}$N has a tunable direct bandgap which varies with Al composition from 3.4 eV (GaN) to 6.2 eV (AlN). This feature makes Al$_x$Ga$_{1-x}$N a good candidate of emission materials in ultraviolet emitting devices covering UV-A (400nm-320nm), UV-B (320nm-280nm), and UV-C (280nm-200nm). Alternatively, Al$_x$Ga$_{1-x}$N can be used for solar blind ultraviolet detectors due to its proper bandgap, which corresponds to wavelength from 365nm to 200nm. Furthermore, Al$_x$Ga$_{1-x}$N has good electrical properties including high breakdown field strength and saturation electron drift velocity, leading to outstanding application performance in semiconductor power devices and high speed transistors. Finally, the high quality Al$_x$Ga$_{1-x}$N material can also be used as substrates for the growth of III-V group semiconductors.

To obtain high quality Al$_x$Ga$_{1-x}$N films, metal organic chemical vapor deposition (MOCVD), molecular beam epitaxy (MBE), and pulsed laser deposition (PLD) are the mostly used technologies. Nevertheless, these technologies are expensive, dangerous, and low yield. They are suitable for very thin film growth aiming at scientific research in laboratory instead of massive production. In this regard, magnetron sputtering is a promising alternative technology for the growth of Al$_x$Ga$_{1-x}$N. However, while AlN and GaN semiconductor films with good quality have been grown successfully using magnetron sputtering, there is less reports of using this technology to grow Al$_x$Ga$_{1-x}$N at present. This work tries to fill this gap between Al$_x$Ga$_{1-x}$N growth and magnetron...
sputtering by studying the growth condition of Al$_x$Ga$_{1-x}$N films using radio frequency (RF) magnetron sputter equipment.

2. Experimental
Al$_x$Ga$_{1-x}$N films were deposited on Si (111) wafers using RF magnetron sputtering. The substrates were ultrasonically cleaned with acetone, ethanol, and deionized water to remove surface stains, and then treated by O$_2$ plasma in plasma cleaner. A Al$_{0.6}$Ga$_{0.4}$N target with 99.99% purity was used for the sputtering in Argon (Ar) and Nitrogen (N$_2$) mixed atmosphere. The RF power was fixed to be 45W. Prior to deposition, the chamber was evacuated to a pressure of 5×10$^{-4}$ Pa. The target was cleaned by Ar$^+$ bombardment for 10 mins. The deposition was block by a shutter above the substrate until the sputtering rate was stabilized. The growth time was set to be 3 hours. Based on the above recipe, the Al$_x$Ga$_{1-x}$N film deposition was conducted with either variable pressure or N$_2$ concentration, producing two groups of samples. For the first group, the N$_2$ concentration was set to be 33 % (volume ratio), while the total pressure in the chamber varied from 0.8 Pa to 1.6 Pa. The second group was about N$_2$ concentrations, which was adjusted across the desired condition. The deposition process is illustrated in Fig.1.

The crystalline structure was characterized using X-ray diffractometer (XRD, Rigaku Ultima IV). The surface morphology and the cross section of the films were observed by scanning electron microscope (SEM, SU3500). The elemental compositions of samples were detected using Energy-dispersive X-ray spectroscope (EDS, JSM-5910LV). The atomic force microscope (AFM, Bruker) was used to determine surface roughness of films.

3. Results and discussion

3.1 Influence of sputtering pressure on the texture of Al$_x$Ga$_{1-x}$N films

Fig.2 XRD spectra of Al$_x$Ga$_{1-x}$N films with different sputtering pressure.
Fig. 2 shows the XRD spectra of Al\textsubscript{x}Ga\textsubscript{1-x}N films deposited at a sputtering power of 45W and 33% N\textsubscript{2} with sputtering pressure of 0.8 Pa, 1.0 Pa, 1.2 Pa, and 1.6 Pa. According to PDF#25-1133 and #50-0792 diffraction cards, the 2θ of AlN (004) and GaN (004) are 76.4° and 72.9°, respectively. We can infer that the diffraction peak of 75.7° on the graph is Al\textsubscript{x}Ga\textsubscript{1-x}N (004). Only (004) peak can be found in the measured range, indicating that the film was grown with the (004) plane parallel with the substrate. Fig. 2 shows that the pressure is 1.0 Pa, which has the highest diffraction peak. With the pressure increasing, the mean free path of the sputtered particles was shortened in the chamber. The sputtered particles would experience more gas scattering before arriving at the substrate surface with most of their kinetic energy dissipated. Hence, it is difficult to rearrange the atoms on the substrates.

![Fig. 2 XRD spectra of Al\textsubscript{x}Ga\textsubscript{1-x}N films deposited at different pressures.](image)

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The EDS spectrum of the film grown at 1.0 Pa is showed in Fig. 3. The EDS results of all four films show the existence of Al, Ga and N elements, confirming the Al\textsubscript{x}Ga\textsubscript{1-x}N composition. The atom ratio of Al to Ga of the sample of 0.1 Pa is 3:1. This value of the target is 3:2. The high Al concentration in the film can be ascribed to that Al atoms are easier to combine with N than Ga since the Al-N bond energy is 2.88 eV, and Ga-N bond energy is 2.2 eV. During the film deposition, Al atoms are more competitive than Ga atoms, resulting in an increase in Al composition in the Al\textsubscript{x}Ga\textsubscript{1-x}N films.

![Fig. 3 EDS spectrum of Al\textsubscript{x}Ga\textsubscript{1-x}N film grown at 1.0 Pa.](image)

Fig. 3 The EDS results of Al\textsubscript{x}Ga\textsubscript{1-x}N film grown at 1.0 Pa.

Fig. 4 shows the SEM images of Al\textsubscript{x}Ga\textsubscript{1-x}N films deposited at 0.8 Pa, 1.0 Pa, 1.2 Pa, and 1.6 Pa. As the pressure increases, the morphology of the films changes from columnar to more uniform and compact structure. This is because the mean free path of the sputtered particles increases with the increase of pressure, allowing more time for gas scattering and leading to a more compact growth of the films.

![Fig. 4 SEM images of Al\textsubscript{x}Ga\textsubscript{1-x}N films.](image)

Fig. 4 SEM image for Al\textsubscript{x}Ga\textsubscript{1-x}N films of (a) 0.8 Pa, (b) 1.0 Pa, (c) 1.2 Pa, (d) 1.6 Pa.
SEM images of Al\textsubscript{x}Ga\textsubscript{1-x}N thin films grown at various pressures are shown in Fig. 4. Increasing pressure from 0.8 to 1.0 Pa results in the decreasing of defects. Further increase of the pressure induces defects on the surface of the samples. The defects appear as bubbles and become larger as the pressure increases. The cause of the defects can be explained considering the growth mechanism. The sputtered Al, Ga and N atoms from target converge on substrate surface. At the early stage of growth, these atoms will first form a cluster. After that, more atoms will gather around the cluster and then crystalize based on the cluster sequentially. If the sputtering pressure is too high, for example, 1.6 Pa, the atoms that reach the substrate will not have enough energy to rearrange, and thus forming defects in the films. In addition, there is a large lattice mismatch and thermal mismatch between the Si (111) and the Al\textsubscript{x}Ga\textsubscript{1-x}N films. With the growth time prolonged, these defects will be further amplified. From the results of SEM, the optimum growth pressure is 1.0 Pa, which produced no obvious bubbles on the film surface.

Fig. 5 AFM images (10µm×10µm) of Al\textsubscript{x}Ga\textsubscript{1-x}N films of (a) 0.8 Pa, (b) 1.0 Pa, (c) 1.2 Pa, (d) 1.6 Pa; (e): \(R_q\) and \(R_a\) along with pressures. The data are extracted from the AFM images.
The 3D AFM images (10µm×10µm) of the films grown under different pressure are shown in Fig 5. In general, the values of the Rq (root mean square of roughness) and Ra (average roughness) increase as the pressure increases. At 1.0 Pa, the roughness of the AlxGa1-xN film is the lowest, with Rq=1.01 nm and Ra=0.71 nm. So, the best sputtering pressure can be nailed down to be 1.0 Pa, which is consistent with SEM analysis.

3.2 Influence of growth atmosphere on the texture of AlxGa1-xN films

Fig.6 XRD spectra of AlxGa1-xN films grown in atmospheres with N2 proportions.

Fig.6 shows the XRD Patterns of AlxGa1-xN films deposited in atmospheres with different N2 proportions with a sputtering pressure of 1.0 Pa and a fixed power of 45W. All the samples were found to have AlxGa1-xN (004) in the measured range except for the diffraction peak from the Si substrate. The (004) peak for 33% N2 has the most strong intensity. The reason is that since the sputtering pressure is constant, increasing N2 proportion means reducing the Ar+. And reducing the Ar+ will directly decrease the sputtering yield of the target. So, an atmosphere of lower N2 proportion means that the Al and Ga Particles are of higher kinetic energies to transfer to the substrate for crystallization. If the nitrogen concentration is lower, firstly, enough N atoms cannot be supplied into the chamber. Secondly, during the experiments, it was found that when the nitrogen concentration is too low, Ar+ will carry more energy. Although this energy cannot cause the target to crack, the surface of the target becomes black.
Fig. 7 SEM image of Al\(_x\)Ga\(_{1-x}\)N films grown in atmospheres with N\(_2\) proportions of (a) 20\%, (b) 33\%, (c) 43\%, (d) 50\%.

N\(_2\) proportion in atmosphere is a key factor affecting film quality. The surface morphology of the films grown in atmospheres with N\(_2\) proportions of 20\%, 33\%, 43\%, and 50\% are shown in the Fig. 7. With high N\(_2\) proportion of 43\% and 50\%, lots of bubbles appear on the surface of the samples. In contrast, the Al\(_x\)Ga\(_{1-x}\)N film of 33\% N\(_2\) proportion does not have obvious defects. We speculate that high nitrogen concentration would lead to the reduction of ionized Ar\(^+\). Therefore, the energy bombarding the target is reduced, and the energy of the sputtered target atoms is reduced. Insufficient atomic energy would lead to defects. Hence, the optimal N\(_2\) proportion should be around 33\%. 
Fig. 8 is the AFM characteristics of Al\textsubscript{x}Ga\textsubscript{1-x}N films grown in different atmospheres. The R\textsubscript{q} and R\textsubscript{a} of the film of 33\% N\textsubscript{2} proportion is smallest, indicating for a consistent conclusion with the SEM analysis, that is, the atmosphere with 33\% N\textsubscript{2} proportion is the best growth condition for Al\textsubscript{x}Ga\textsubscript{1-x}N film.

The cross-section SEM image of the Al\textsubscript{x}Ga\textsubscript{1-x}N film grown in atmosphere with N\textsubscript{2} proportion of 33\% is shown in Fig. 9. The film thickness was measured to be ~250 nm. It is worth of noting that to attain this thickness, the growth lasted three hours. The deposition speed is expected to be increased by increase the sputtering power, which would bring about the demand of high-quality target that can sustain under a high power.

4. Conclusions

In summary, RF magnetron sputtering technique was used to deposit Al\textsubscript{x}Ga\textsubscript{1-x}N films. The XRD results showed the films grew with a [004] orientation. The EDS results revealed the higher Al content
in the film than the target, which was ascribed to that the higher Al-N bond energy than Ga-N induced a preferred Al integration. The influences of sputtering pressure and N₂ proportion in the atmosphere on the film quality were investigated for an optimized growth condition. It was revealed that both high sputtering pressure and high N₂ proportion in the atmosphere would deteriorate the quality of the AlₓGa₁₋ₓN films. The best parameters were ascertained, which are the sputtering pressure of 1.0 Pa and N₂ proportion of 33% in the atmosphere. At the end of the article, it is proposed to improve the quality of the target to improve the deposition speed. These explorations can provide a reference for the development of magnetron sputtering deposition technique of high quality AlₓGa₁₋ₓN films.

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