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Study of AlN Films Doped by Si Thermal Diffusion

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Abstract: This paper deals with the characteristics of aluminium nitride (AlN) films doped by silicon (Si) thermal diffusion. The films are analyzed by energy dispersive X-ray spectroscopy (EDS) and high-temperature dependent electrical conductivity. The results of EDS show that the Si element is successfully doped into the AlN films using SiN_x as the diffusion source at the temperature of 1 250 ℃. The high-temperature current-voltage (*I-V*) measurements show that the electrical properties of the AlN films can be prominently improved by Si thermal diffusion, and at the measured temperature of 460 ℃ their electrical conductivities increase from 1.9×10^{-3} S·m^{-1} to 2.1×10^{-2} S·m^{-1} after the Si thermal diffusion. The high-temperature dependence of thermal conductivity suggests that the activation energies of V_N^{3+} and Si are about 1.03 eV and 0.45 eV, respectively.

Key words: impurities; nitrides; thermal diffusion
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氮化铝薄膜的硅热扩散掺杂研究

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摘要：采用热扩散方法，对 AlN 薄膜进行了 Si 掺杂。利用电子能量散射谱(EDS)以及高温变温电导对薄膜进行了分析。EDS 测试结果表明：在 1 250 ℃的温度下，氮化硅(SiN_x)作为 Si 的扩散源，可以实现对 AlN 薄膜的 Si 热扩散掺杂。高温电流-电压(*I-V*)测试表明：在 460 ℃测试温度下，AlN 薄膜在热扩散掺杂以后，其电导从 1.9×10^{-3} S·m^{-1}增加到 2.1×10^{-2} S·m^{-1}。高温变温电导测试表明：氮空位(V_N^{3+})和 Si 在 AlN 中的激活能为 1.03 eV 和 0.45 eV。

关　键　词：杂质；氮化物；热扩散

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1 Introduction

In recent years, AlN has attracted more and more attentions due to its outstanding physical and chemical properties. AlN, a direct transition-type semiconductor with the bandgap of about 6.14 eV at room temperature, shows high thermal conductivity, high breakdown voltage, and good thermal stability[1-2]. These properties will make AlN suitable for the fabrication of ultraviolet photoelectric devices, as well as high-temperature and high-power electronic devices. In order to realize these devices, it is necessary to obtain n-type and p-type AlN. Si may be a promising candidate for the donor impurities of AlN, it has been proved to be an effective donor of $Al_xGa_{1-x}N$[2]. However, according to the theoretical studies, n-type doping is inhibited by the low formation energy of Al vacancies (V_{Al}) in n-type AlN, and these vacancies acting as triply charged acceptors can compensate the Si donors[3-4]. Recently, conductive Si-doped AlN has been achieved by in-situ and ion-implantation doping, and their results suggest that the insulating nature of AlN is related to the presence of oxygen (O) rather than to the formation of V_{Al}[5-6]. Indeed, due to the difficulties to the growth of high quality AlN films, the high ionization energy of Si donor, and the compensation by native defects and unintentionally incorporated background impurities, a number of contradictory results about the bulk properties and transport phenomena of Si-doped AlN have been published. Furthermore, according to reports the group-Ⅲ nitrides are very chemically inert, and the diffusion coefficients of impurity species are extremely low[7]. This implies that it is tough to obtain n-type AlN by Si thermal diffusion. Actually, to the best of our knowledge there have been little works concerning the characteristics of AlN doped by Si thermal diffusion.

In the present work, the AlN films doped by Si thermal diffusion are first demonstrated, and the effects of Si doping on their electrical properties are studied in detail.

2 Experiments

A 1-μm-thick unintentionally doped wurtzite AlN film was grown by metal organic vapor phase epitaxy (MOCVD) on a polished optical-grade *c*-face (0001) sapphire substrate. Trimethylaluminum (TMAl) and ammonia (NH_3) were used as the aluminium (Al) and nitrogen (N) source, respectively. The carrier gas was hydrogen (H_2), and the growth pressure was kept at 1.1×10^4 Pa. First of all, an AlN buffer layer was grown on the sapphire substrate at the temperature of 500 ℃, which was greatly lower than the temperature of AlN epitaxial layer. Once the buffer layer was grown, the tempe-rature was raised to 1 150 ℃ to grow the AlN epitaxial layer. After the AlN epitaxial layer was grown, it was diced into 10 mm × 10 mm sizes. Before preparing for the Si thermal diffusion all specimens were cleaned sequentially in an ultrasonic bath with acetone, alcohol and deionized water for 15 min in order to remove any organic and inorganic surface contamination, and then they were dried thoroughly using the nitrogen gas (N_2). A 250-nm-thick Si layer as a diffusion source was deposited on one AlN film by direct current (DC) magnetron sputtering at room temperature, and then a 150-nm-thick SiN_x layer was deposited on the Si layer to serve as a cap by DC reactive magnetron sputtering. On another AlN film, a 150-nm-thick SiN_x layer was only deposited to serve as a diffusion source. These two films were annealed at the temperature of 1 250 ℃ for 55 h in an N_2 atmosphere at a pressure of about 1.5×10^5 Pa. The film with the diffusion source of SiN_x was labeled sample A, and the other film was labeled sample B. An AlN film without the diffusion source was also annealed at the same conditions, and it was labeled sample C. In order to compare experiment results, an AlN film without experience of annealing was also measured and labeled sample D. After annealing, the SiN_x and Si layer were etched off in dilute HF (49%) and etching solution [$V(HF):V(HNO_3):V(H_2O)=1:1:2$], respectively. Finally, Ti/Al (20 nm/200 nm) electrodes were formed by electron beam evaporation and subsequently annealed at the temperature of 600 ℃ for 7 min in N_2 atmosphere in order to reduce the electrical contact resistances. The radial of metal contact pad was 0.5 mm, and the gap between two contact pads was 5 mm. These parameters of electrodes were used to calculate the electrical conductivities of all samples.

The crystalline structure of the grown AlN film was examined by an X-ray diffractometer (XRD) (D8Discover, Bruker, Germany). The profiles of Si element in samples were analyzed by energy dispersive X-ray spectroscopy (EDS) equipped on a field emission scanning electron microscopy (SEM) (HITACHI S-4800, Japan), and their electrical properties were characterized by Varying high-temperature current-voltage (KEITHLEY model 237, America).

3 Results and Discussion

The XRD measurement at $\theta/2\theta$ configuration is used to characterize the crystal quality of AlN film, and the results for (0002) plane scan are shown in Fig. 1. From the figure it can be observed that the diffraction peak has a symmetric shape, and its full width at half maximum (FWHM) is found to be about 135 arcsec by using the Lorentz function to fit the measured data. These results clearly indicate that the grown AlN film has a good crystalline quality.

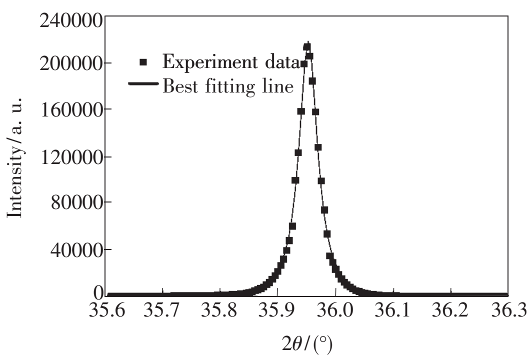

Fig. 1 XRD patterns of AlN film grown on sapphire substrates by MOCVD

In order to verify whether the Si element is successfully diffused into the AlN films by thermal diffusion, EDS operating in scanning mode long the surface normal over the cross-section of samples is used to characterize the profiles of Si element, and the results are shown in Fig. 2. Inspection of the figure clearly reveals that the Si element is only observed on the near-surface region of sample A, which implies that the SiN_x as the diffusion source is conducive to the diffusion of Si into AlN. This phenomenon can be attributed to the following facts. H. Ogata *et al.* have found that the diffusion coefficient of Al in silicon nitride (Si_3N_4) is greatly larger than that of Al in silicon[8]. This indicates that the exchange of Al and Si on the interface of AlN and SiN_x film may be greatly faster than that on the interface of AlN and Si film. Furthermore, the SiN_x layer used in our experiment is amorphous and non-stoichiometrical, which can further promote the exchange of Al and Si on the interface of AlN and SiN_x film due to the unsaturated bounds of Si and N atoms in the SiN_x layer. Lastly, the annealing temperature (1 250 ℃) is greatly higher than the decomposition temperature (1 040 ℃) of AlN, which can further promote the exchange of Si and Al on the interface of SiN_x and AlN film. These may be why the Si element is only observed on the near-surface region of sample A in the EDS analyses. It is worth mentioning that the purpose of using EDS rather than secondary ion mass spectrometer (SIMS) to analyze the depth profiling of Si is to qualitatively verify whether the Si is successfully diffused into the AlN film by thermal diffusion.

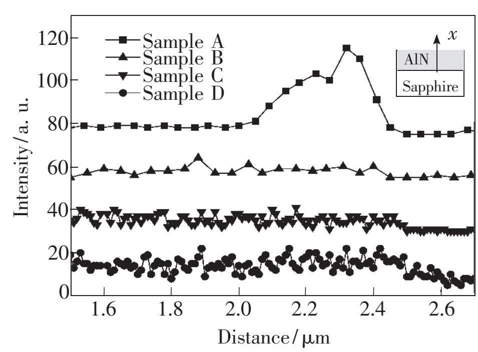

Fig. 2 EDS analyses of Si on the near-surface region of samples. The inset is the cross-section of the samples, and the arrow also indicates the scanning direction.

It is well known that the impurity has a strong influence on electrical properties of semiconductors, and the electrical conductivity is one of the best parameters to characterize the electrical properties of the semiconductor whose resistivity is too large to be characterized by Hall-effect measurements. The current-voltage (*I-V*) measurements at the temperature of 460 ℃ are used to characterize the electrical properties of all samples, and the results are shown in Fig. 3. It can be observed that the *I-V* curves of sample B and C nearly coincide with that of sample D. This means that the annealing temperature nearly has no effects on the electrical properties of AlN films, even the annealing temperature is greatly higher than the decomposition temperature of AlN. The calculated electrical conductivities are about 2.5×10^{-3}, 2.3×10^{-3} and 1.9×10^{-3} S · m^{-1} for sample B, C and D. However, it is surprised that the *I-V* curve of sample A exhibits a sharper linear *I-V* curve, which indicates that the electrical conductivity of sample A is greatly larger than that of the other three samples. The calculated electrical conductivity is about 2.1×10^{-2} S · m^{-1} for sample A. These results clearly show that the electrical properties of AlN films can be prominently improved by Si thermal diffusion.

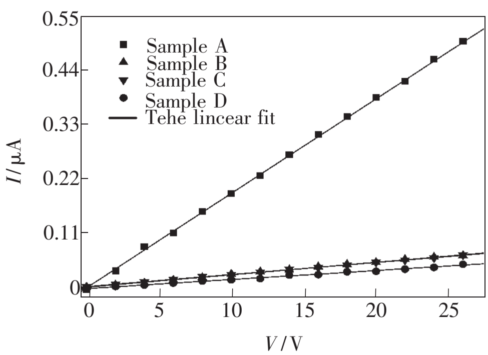

Fig. 3 Current-voltage characteristics of samples at the measured temperature of 460 ℃

Fig. 4 shows the measured high-temperature dependent electrical conductivity of all samples. It can be observed that in the whole temperature range the electrical conductivity of sample A is always larger than that of the other three samples at the same measured temperature, and their electrical conductivities are nearly the same. In order to verify the conduction mechanism of these samples at high temperature, we extract the activation energy of electrical conductivity by fitting the measured high-temperature dependent electrical conductivity using the relation: $\sigma(T) = e\mu(T)n(T)$, where $\sigma(T)$ is the electrical conductivity at temperature T, e is the electron elementary charge, $\mu(T)$ and $n(T)$ are the mobility and the carrier concentration at temperature T. In order to obtain the activation energy of Mg, Nakarmi M L *et al.* have assumed that the temperature dependent mobility is $\mu(T) = \mu_0 T - 3/2$ in Mg-doped AlN films at high temperature, and the obtained activation energy of Mg acceptor agrees well with the value obtained by theoretical calculations and optical measurements[9]. Kanechika M *et al.* have found that the temperature dependent mobility is $\mu(T) = \mu_0 T^{-1.1}$ in Si-doped AlN films at high temperature, and they have considered that the mobility of carriers is limited by the polar optical phonon and point defect scatterings; the Si-doped AlN films used in his experiments are obtained by Si ion-implantation into unintentionally doped AlN films, and lots of point defects are generated in these films[6]. However, more reporters have confirmed from the theories and experiments that at high temperature the mobility of carriers in Si-doped or unintentionally doped AlN films is limited by the polar optical phonon scattering[10-11]. Our experiments are carried out at high temperature, and we assume that the temperature dependent mobility and carrier concentration are $\mu(T) = \mu_0\exp(\hbar\omega/kT)$ and $n(T) = n_0\exp(-E_d/kT)$, where $\hbar\omega$ is the polar phonon energy, E_d is the donor or acceptor activation energy, k is the Boltzmann constant[12]. The results of the least-squares fitting are shown as lines in Fig. 4, and the fitted activation energy values are about 1.01, 1.08 and 0.99 eV for sample B, C and D.

The electrical properties of unintentionally doped AlN films have been believed to be related to residual oxygen (O_N), carbon (C_N) and nitrogen vacancies (V_N). The O_N and V_N can introduce deep level in the band gap and serve as deep donors. The activation energy of O_N is very high, and its value obtained from experiments and theoretical calculations is over 2 eV[13-14]. It is known that there are three types of V_N in AlN to serve as donors. The energy lever of V_N with triple positive charges (V_N^{3+}) is greatly shallower than that of V_N with a single positive charge (V_N^{+}), while the V_N with double positive charges (V_N^{2+}) is unstable[14]. The calculated and measured energy level of V_N^{3+}, comparing with the conduction band, is in the range of 0.9 ~ 1.2 eV, namely the activation energy value of

V_N^{3+} in AlN ranges of 0.9 ~ 1.2 eV[9,15]. The level introduced by CN lies at about 0.5 eV above the valence band edge causing the CN to act as a deep acceptor, meaning that the activation energy value of CN is about 0.5 eV in AlN[4]. Based on the above discussions we conclude that the activation energy extracted from our experiments of sample B, C and D belongs to the V_N^{3+}, and their electrical properties are dominated by the residual V_N^{3+}; the fitted activation energy value agrees reasonably with that of V_N^{3+}. On the other hand, the fitted activation energy values are nearly the same for these three samples, and even the annealing temperature (1 250 ℃) is greatly higher than the decomposition temperature of AlN, which indicates that the electrical properties of AlN films are still dominated by the V_N^{3+} after high temperature annealing in N_2 atmosphere.

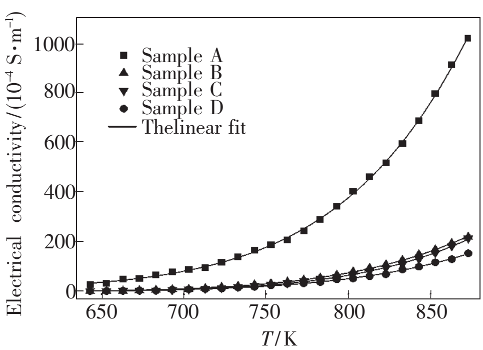

Fig. 4 The electrical conductivity of samples vs. the measured temperature

In the case of sample A, the piecewise fitting is necessary to fit accurately the temperature dependent electrical conductivity in the whole range of measured temperature, which indicates that another energy level is introduced into the band gap after high temperature annealing. One of the fitted activation energy is about 1.03 eV, and the other is about 0.45 eV. Based on the above discussions about the other three samples, we can confirm that the fitted activation energy of 1.03 eV belongs to the V_N^{3+}. The reported activation energy value of Si in Si-doped AlN ranges of 0.06 ~ 0.55 eV, which means that the other activation energy of 0.45 eV can be attributed to the Si[10,16]. Thus, we can confirm that the AlN doping is successfully achieved by Si thermal diffusion in sample A.

While the electrical properties of AlN films can be prominently improved by Si thermal diffusion using SiN_x as the diffusion source, the improvement is not as tremendous as the films doped by in-situ or ion-implantation doping[5-6]. This phenomenon implies that the effects of thermal diffusion doping on electrical properties of AlN are different to that of in-situ or ion-implantation doping. In general, there are two main factors to influence the Si doping efficiency in AlN. The first one is the transition of an impurity from a substitution position to a DX-like state. In this case, the bond between the impurity and one of its first neighbors is broken, and one or both of these two atoms move from substitution sites to interstitial locations. This process is commonly accompanied by a capture of a second electron by the impurity, and a deep level can be introduced in the band gap. In the nitrides there are four possible DX-like states for the group-Ⅳ impurities. In AlN the DX- state is stable for Si, and the SiAl which serves as a deep donor in a DX- configuration can introduce a level of about 1.6 ~ 1.9 eV below the bottom of the conduction band[4,15]. This indicates that the activation energy of SiAl in a DX- configuration is about 1.6 eV to 1.9 eV. The other factor that may affect the Si doping in AlN is self-compensation, *i. e.* the impurity simultaneously incorporates on both cation and anion sublattices. The fact that the improvement in electrical properties of the AlN films doped by Si thermal diffusion doping is not as tremendous as the films doped by in-situ or ion-implantation doping could be attributed to the self-compensation. On the one hand, there are a lot of residual V_N in our AlN films, and these V_N can prove the acceptor sites for Si atoms in the thermal diffusion process, which can enhance the self-compensation of Si in the AlN films. One the other hand, in our experiments the annealing temperature is greatly higher than the decomposition temperature of AlN, which not only can enhance the exchange of Si and Al on the interface of SiN_x and AlN film but also let more N escape from the near-surface region of the AlN film. This means that more V_N can be left to form the acceptor sites for the Si atoms in the near-surface region of the AlN film. In the N-poor region (or Al-rich region) the self-compensation can be further enhanced by some mechanisms such as the formation of nearest-neighbor donor-acceptor pairs[4]. Consequently, the electrical properties of AlN films can be prominently improved by Si thermal diffusion with the diffusion source of SiN_x, whereas the improvement is not as tremendous as the films doped by in-situ or ion-implantation doping.

4 Conclusion

In conclusion, the AlN doped by Si thermal diffusion is demonstrated in this paper. The films are analyzed by energy dispersive X-ray spectroscopy (EDS) and high-temperature dependent electrical conductivity. The results of EDS show that the Si element is successfully doped into the AlN film using SiN_x as the diffusion source at the temperature of 1 250 ℃. The high-temperature current-voltage (*I*-*V*) measurements show that the electrical properties of the AlN film can be prominently improved by Si thermal diffusion, and at the measured temperature of 460 ℃ its electrical conductivity increases from 1.9×10^{-3} S·m^{-1} to 2.1×10^{-2} S·m^{-1} after the Si thermal diffusion. The high-temperature dependence of electrical conductivity suggests that the electrical properties of unintentionally doped AlN film are dominated by the residual V_N^{3+}, and the activation energies of V_N^{3+} and Si are about 1.03 eV and 0.45 eV respectively.

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