Luminescence spectroscopy of ion implanted AlN bulk single crystal

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Abstract: High concentrations of Si and Zn were implanted into (0001) AlN bulk crystal grown by the self-seeded physical vapor transport (PVT) method. Cathode luminescence (CL) and photoluminescence (PL) spectroscopy were used to investigate the defects and properties of the implanted AlN. PL spectra of the implanted AlN are dominated by a broad near-band luminescence peak between 200 and 254 nm. After high temperature annealing, implantation induced lattice damages are recovered and the PL intensity increases significantly, suggesting that the implanted impurity Si and Zn occupy lattice site of Al. CL results imply that a 457 nm peak is Al vacancy related. Resistance of the AlN samples is still very high after annealing, indicating a low electrical activation efficiency of the impurity in AlN single crystal.

Key words: AlN; implantation; impurity; defect

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1. Introduction

AlN single crystal is an important substrate for the epitaxial growth of high quality Ⅲ-nitride materials and development of novel hetero-junction devices. Its excellent optical, electrical and thermal conductivity properties make it an ideal material for high brightness blue diodes, ultraviolet light-emitting diodes, laser diodes, surface acoustic waves (SAWs), solar-blind ultraviolet (UV) detectors and high-frequency high-pressure converters[1,2]. Since the original non-doped AlN single crystal is an insulator, N-type and P-type doping methods for the preparation of low-resistance AlN have to be solved in order to meet the demands of optoelectronic device manufacture[3–6]. So far, the doping technology of AlN single crystal is not yet settled, and the doping related defects and activation mechanism require a large amount of in-depth study. In this paper, AlN single crystal was implanted with a high concentration (10^{19} cm^{-3}) of Si and Zn to study doping and activation of donor and acceptor impurities in AlN single crystal. Both CL and PL were used to analyze the defects and properties of the implanted samples. The results indicate that implantation induced defects are suppressed and implanted impurities are activated after annealing at high temperature. The resistivity of the impurity implanted and annealed AlN is still very high (> 10^{11} Ω·cm), which is ascribed to the very low activation efficiency and strong defect compensation effect of the impurities in AlN. Therefore, a higher doping concentration (10^{20} cm^{-3} or even higher) and a defect control technique are needed in order to obtain low-resistivity AlN.

2. Experimental details

Self-nucleated AlN crystal boules of 45 mm diameter were grown by the physical vapor transport (PVT) method in our laboratory[2]. After slicing, (0001) oriented AlN single crystal wafers with sizes of 5–8 mm were selected for ion implantation under 500 keV in our institute. Impurities of Si, Mg and Zn with an ion dose of about 5×10^{14} cm^{-2} were implanted into the samples, respectively. The concentration of impurities implanted is defined with the formula $n(x) = \frac{S}{\sqrt{2\pi}\sigma_p} \exp[-\frac{(x-R_p)^2}{2\sigma_p^2}]$, where $n(x)$ is the concentration of the impurities, S is the injection rate per unit area, R_p is the projected range, and σ_p is the projected straggle[7]. Thus, a layer of about 1000 Å with Si, Mg and Zn of 10^{19} cm^{-3} were obtained through the implantation. One sample was selected from each kind of implanted sample for annealing at 1200 °C for 1 h in a medium frequency induction heating furnace under protection of N_2 with pressure of 90.0×10^3 Pa.

CL testing was conducted in a vacuum system at room temperature. The excitation electron energy was about 25 keV and the photon energy detection range was between 2.0–6.2 eV. Deep ultraviolet PL spectra of 4.3–6.53 eV were measured at 79.1 K by using the vacuum ultraviolet spectrometer in the Beijing Synchrotron Radiation Facility, Institute of High Energy Physics, Chinese Academy of Sciences.

3. Results and discussion

Normalized CL spectra of impurity implanted/annealed AlN samples and an as-grown undoped AlN sample are shown

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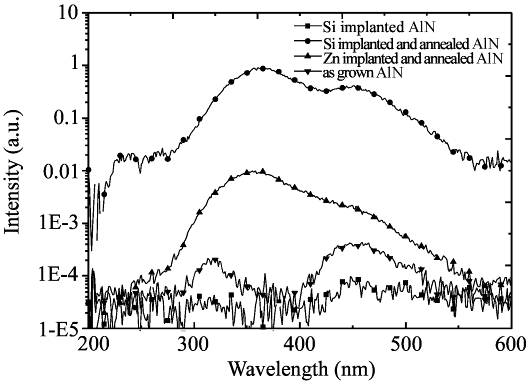

Fig. 1. CL spectra of as-grown undoped AlN single crystal and AlN single crystals implanted with Si and Zn.

in Fig. 1. It is clear that Si- and Zn-implanted and annealed AlN samples have two strong luminescence peaks at 362 and 457 nm, respectively. The as-grown undoped AlN sample also has two similar CL peaks but with weaker intensity. In contrast, luminescence of the as-implanted AlN is the weakest. This fact indicates that there is a high concentration of implantation induced defects acting as non-radiative centers in the as-implanted sample. After high temperature annealing, the defects are suppressed and the lattice damage is recovered.

It is noted that the implanted and annealed samples have a much higher CL intensity than the as-grown sample. This implies that defect concentration is reduced significantly after the annealing treatment of the implanted sample. It is apparent that the 457 nm peak relative intensity of the implanted sample becomes weak after the annealing, as compared to the as-grown sample and the as-implanted sample. Since both Si and Zn occupy Al sites in the AlN crystal lattice, it is reasonably argued that the 457 nm peak is Al vacancy related. With the implantation and thermal activation of Si and Zn in AlN single crystal, Al vacancy defect is suppressed effectively. In addition, Si and Zn usually act as a shallow donor and a shallow acceptor in AlN, respectively, and they will contribute more free carriers after thermal activation. This is also an important reason that the implanted and annealed samples have higher CL intensity.

From Fig. 1 it is seen that the CL intensity of the Si-implanted sample is also much higher than that of the Zn-implanted. It is well-known that p-type doping is more difficult than n-type doping in wide gap semiconductors. It is expected that the inherent defect compensation effect of the Zn-implanted and annealed AlN is more significant, compared to Si-implanted AlN. As a result, luminescence intensity is low due to the existence of non-radiative defects. Similar phenomena also exist in other wide gap semiconductors, such as GaN, InN and ZnO[8]. Thus, it is important to control the compensation defects for the realization of reliable p-type doping of the materials[9].

Since the CL spectrometer is unable to give a satisfactory signal in the deep ultraviolet region, we use the vacuum ultraviolet spectrometer to study the band edge PL of the implanted AlN samples; the results are shown in Fig. 2. It is shown that

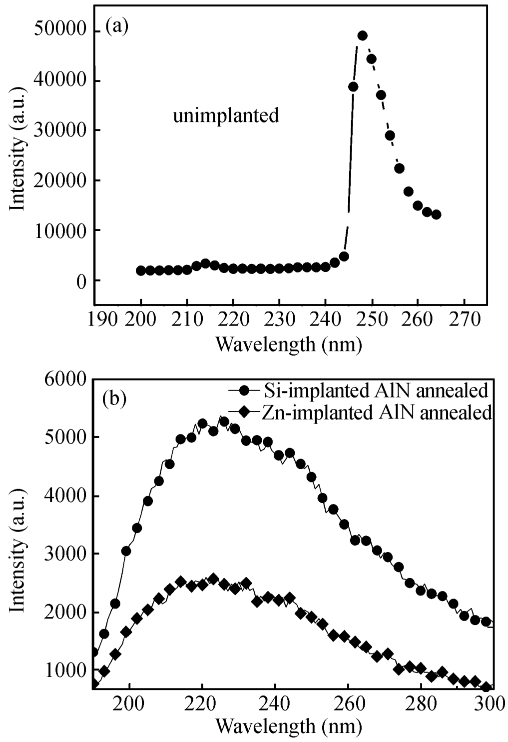

Fig. 2. PL spectra of AlN single crystal: (a) Original AlN; (b) Si- and Zn-implanted and annealed.

the implanted and annealed samples have a very broad band edge luminescence from 200 to 254 nm, while the as-grown undoped AlN single crystal exhibits a single narrow peak. It is expected that implantation induced lattice defects still exist after a high concentration of Si or Zn is implanted into AlN and after high temperature annealing. Both the high concentration impurity and the defect are responsible for the broad band edge luminescence. In addition, we speculate that the redshift of the center-left peak in Fig. 1(a) might be due to the activation of substitutional Si atoms, which results in an impurity energy level drop of about 0.52 eV. From the PL spectra we can see that the strongest peak is in the vicinity of 220 nm, and the drop of impurity energy level is hereby figured out as about 0.56 eV. This coincides well with the CL results.

The formation of the center-left peak in AlN is believed to be caused by an oxygen defect cluster, which leads to the emergence of the impurity energy level[10, 11]. The structure of the defect cluster changes when the doped atoms replace the location of Al-bit, making the impurity energy level shift. Unfortunately, the structure of the defect cluster is still unclear.

The 457 nm emission peak corresponds to a photon energy of about 2.71 eV, indicating that the defect is at a deep level located near the central band. From Fig. 1 we can find out that the emission peak remains the same after annealing. This implies that these defects are intrinsic defects of AlN crystal. The existence of the defects significantly enhances the carrier electrical compensation and limits the increase of carrier concentration. Hall measurement reveals that the implanted and annealed samples are still insulators with resistivity exceeding the scope of the measurement system. Therefore, the resistivity can only be estimated to be over 10^{11} Ω·cm. The present results also suggest that the defects in AlN have a very high thermal stability. In addition, since the energy levels of Si, Zn and Mg in AlN single crystal are about 200–300 meV below conduction band edge or above valence band edge[12−15], their electrical activation efficiency is destined to be very low. Therefore, further increase of the implantation concentration and defect control are needed in order to obtain low-resistance AlN single crystal materials.

4. Conclusions

High temperature annealing effectively removes defects generated by Si, Zn ion implantation in AlN single crystal, activates the substitutional impurity atoms and reduces the concentration of Al vacancy related defects. Further substantial increase of the implantation concentration and control of deep level defects are necessary in order to obtain low-resistance AlN single crystal materials.

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