Investigation on microstructure evolution of oxidized Ni/Au ohmic contacts to p-GaN by XRD

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The microstructure evolution of oxidized Ni (20nm)/Au (20nm) contact to p-GaN with increasing annealing temperature was studied by synchrotron x-ray diffraction (XRD) and powder XRD. With the increase of annealing temperature, it was observed that the Au on the p-GaN gradually grew on the p-GaN with the orientation relationship of Au(111)//GaN(0002). NiO also had such a orientation relationship of NiO(111)//GaN(0002) at 500℃ and gradually turned back to polycrystalline structure at higher temperature. The orientation relationship of Au , NiO and GaN implied that the epitaxial crystallization might occur during annealing. The specific contact resistance also reduced to the minimum at 500℃. Therefore, plausibly the epitaxial crystallization is an important mechanism for lowering the contact resistance between oxidized Ni/Au contacts and p-GaN.

1. Introduction

The III-V nitride semiconductors have been extensively investigated for the short wavelength optoelectronic applications [1-2]. For light emitting diodes (LEDs) and laser diodes (LDs), the preparation of low resistance contacts to *p*-type layers is a rather challenging task. It has been reported that Au/Ni based bilayer structures annealed in an oxygen containing ambient are capable of forming ohmic contacts to *p*-GaN with a specific contact resistance in the range of 10^{-2} to 10^{-6} Ωcm^2[5-8.]

Recently, extensive works on the microstructure of the oxidized Ni/Au ohmic contact to p-GaN have been reported [5, 7,10]. The results of transmission electron microscope (TEM) shows that the Ni/Au contact was formed by the Au islands, the amorphous Ni-Ga-O contacting to the p-GaN and a continuous NiO on the top when it was oxidized in air at 500℃. However, the microstructure evolution of the oxidized Ni/Au layers in oxidation process remains unclear yet. The images of the structural evolution are required to understand the ohmic mechanism. Synchrotron x-ray diffraction is a very effective tool to study the structure of thin film due to its good monochromaticity and strong intensity. Since the strong x rays fully penetrate into the film, information on the internal atomic layer structure as well as the buried film-substrate interface is probed. In this work, we focus on the effect of annealing temperature on the microstructure of the contacts. Synchrotron x-ray diffraction was used.

2. Experiment procedure

The Mg-doped GaN films were grown by metal organic chemical vapor deposition (MOCVD) on c-plane sapphire substrate. The thickness of Mg-doped GaN layer was 2.5μm. To activate the Mg atom, these samples were annealed for 20 min at 750°C in N_2 ambient. Hall measurement showed that the hole concentration of p-GaN was $1\times 10^{17}cm^{-3}$ typically. The mesa structures for transmission line method (TLM) were patterned by reactive ion etching (RIE) using $Cl_2/Ar/H_2$. The pads were $200\times 200\mu m^2$ in size, and the spacings were 7, 12, 17, 22, 33, and 37 μm. Prior to deposition of the metal films, the TLM-patterned samples were dipped into HCl:H_2O(1:1) for 1min to remove the native surface oxides. The Ni(20nm)/Au(20nm) bilayer was deposited by an electron beam evaporation system with the base pressure of 4.3×10^{-8}mbarr. Then the Au/Ni/p-GaN specimens were annealed in a rapid thermal annealing system at temperature ranged from 350 to 700℃ for 10min in air ambient. The current-voltage (I-V) characteristics of the contacts were examined on the pads with the spacing of 37μm. The specific contact resistance (ρ_c) was measured by TLM. Synchrotron x-ray diffraction (XRD) was performed in two kinds of modes on the samples. Figure1 shows the two kinds of modes: Mode A, scan with fixed small incident angle; Mode B, scan along the surface normal direction by the linkage of axes of ω and 2θ. Mode A was used to observe the planes not parallel with the surface of p-GaN. In contrast, Mode B was used to observe the planes parallel with the surface of p-GaN. Regular powder XRD was also performed on the samples due to its sensitivity to detect the polycrystalline phases.

3. Results and discussion

Figure 2 shows the I-V characteristics of the Ni(20nm)/Au(20nm) contacts to p-GaN. The samples were annealed at various temperatures from 350℃ to 700℃ in air. The I-V curves show nonlinear property for the as-deposited samples, indicating that the contacts were rectifying. When the annealing temperature was higher than 350℃, the I-V curves became linear, implying that an ohmic contact to p-GaN was formed. And the slopes rose with the increasing annealing temperature at first. However, above 500℃, the slopes of the I-V curves began to decrease. For samples annealed at 700℃, the I-V curves became nonlinear again. Therefore, it was shown that the contact properties strongly rely on annealing temperature.

Figure 3 shows the variation of specific contact resistance as a function of annealing temperature in air. The ρ_c was $6.87\times 10^{-2}\ \Omega cm^2$ at 350℃. It sharply decreased to $2.73\times 10^{-4}\Omega cm^2$ when the annealing temperature increased to 500℃. Above 500℃ the ρ_c began to increase and reached to $6.89\times 10^{-2}\ \Omega cm^2$ at 700℃.

Synchrotron XRD was performed with the mode A and B for the as-deposited and 700℃-annealed samples. Figure 4 showed the difference between Mode A and Mode B. In the as-grown samples, the Au(111) peak was observed in the scan of Mode A and was very weak in the scan of Mode B, indicating that the Au(111) planes in the as-grown samples was not parallel with GaN(0002) planes. Therefore the Au in the as-deposited contact was mainly polycrystalline, or at least was not epitaxial on the p-GaN. In contrast, the Au(111) peak in the 700℃-annealed samples disappeared in the scan of Mode A while it was observed in the scan of Mode B, indicating that the annealing process may remarkably cause Au(111) planes parallel to GaN(0002) planes. Therefore, it was implied that annealing process notably improved the epitaxial structure of the Au film on a GaN layer [9] and the epitaxial relationships for Au/GaN are Au(111)//GaN(0002).

Figure 6 shows the microstructure evolution of the Ni/Au contacts by the synchrotron XRD (Mode A) and the powder XRD (Mode B) profiles respectively. In the synchrotron XRD profiles, as shown in figure 6 (a), the Au (111) peaks became stronger as the temperature increased from 350℃ to 450℃, resulting from the increased size of Au grains on the p-GaN at higher temperature. However, at higher temperature above 450℃ Figure 6 (a) shows that the Au(111) peaks became weaker with the increasing of the temperature. In contrast, figure 6 (b) shows that the Au(111) peak kept increasing with the increasing temperature. Such a contrast shows that Au(111) planes gradually turned parallel with GaN(0002) planes, which implies that the Au gradually grow epitaxially on the p-GaN with the orientation relationship of Au(111)//GaN(0001). To verify the epitaxial structure of Au on the p-GaN, the ω-scan of the Au(111) peak was performed along the surface normal direction of the p-GaN. It was observed that Au(111) peak was invisible in the as-deposited samples and appeared in the 500℃-annealed sample, as shown in Figure 5.

At the same time, figure 6 (a) shows that NiO(111) peak had a sharp decrease at 500℃, implying that polycrystalline structure of NiO was restrained at this temperature. In contrast, Figure 6(b) shows that NiO(111) peak increased at 500℃. Therefore, it is implied that NiO also grew epitaxially with the direction relationship of NiO(111)//GaN(0001). Interestingly, NiO(111) peak in Mode A scan became stronger again with the increasing temperature, especially above 550℃. Therefore, it's conjectured that NiO turned to polycrystalline again at higher temperature and epitaxial structure of NiO was not very stable at high temperature. This needs to be verified by other experiments later.

According to the profiles of the XRD, it is suggested that the epitaxial structure of Au and NiO became dominant at 500℃. The direction relationship was NiO(111)//Au(111)//GaN(0002). Such an epitaxial structure of Au and NiO causes the ρ_c to sharply decrease further at 500℃, as is shown in Figure 4. Narayan et al. confirmed the importance of epitaxial composite structure in achieving low-resistivity ohmic contacts by investigating the low-resistance ohmic contact of Au/Ni/Au to p-GaN [9]. At 600°C the intensity of the Au(111) peaks was the strongest, but the ρ_c at this temperature was not the lowest. An explanation is that more voids were formed between the contact and the p-GaN due to the dissociated Nitrogen from the interface reaction at higher temperatures. These voids separated the crystallized NiO and Au from p-GaN and reduced the contacting area [10].

The shifts of Au(111) peaks were also observed, as shown in figure 6. First, Au(111) peak shifts toward a higher angle by 0.48° at 350℃(it's not shown in Figure6 (a)).This means that the interdiffusion between Au and Ni occurred during annealing, forming Au-Ni solid solutions. Since Ni has smaller atom radius than Au, Au(111) peak shifted to higher angle. Then, the shift of Au(111) peak decreased greatly at 450℃, indicating that most of Ni in the Au-Ni solid solution was driven out again. An explanation is that the formation of NiO is more preferred than Au-Ni solid solution in terms of thermodynamics. Above 450℃, the Au(111) peaks slightly shifted towards higher angle again. This can be explained with the formation of Au-Ga solid solutions[11].

4. Conclusion

Microstructure of oxidized Ni(20nm)/Au(20nm) contacts to p-GaN was studied by synchrotron x-ray diffraction (XRD) and regular powder XRD in this work. The oxidization of the Ni/Au contacts caused Au to change from polycrystalline to monocrystalline-like structure on p-GaN with the increasing of the temperature. NiO also formed monocrystalline-like structure on p-GaN at 500℃. The orientation relationship was NiO(111)//Au(111)//GaN(0002). It suggests that the epitaxial microstructure of Au and NiO was formed, which was an important mechanism to lower the specific contact resistance of oxidized Ni/Au contacts to p-GaN.

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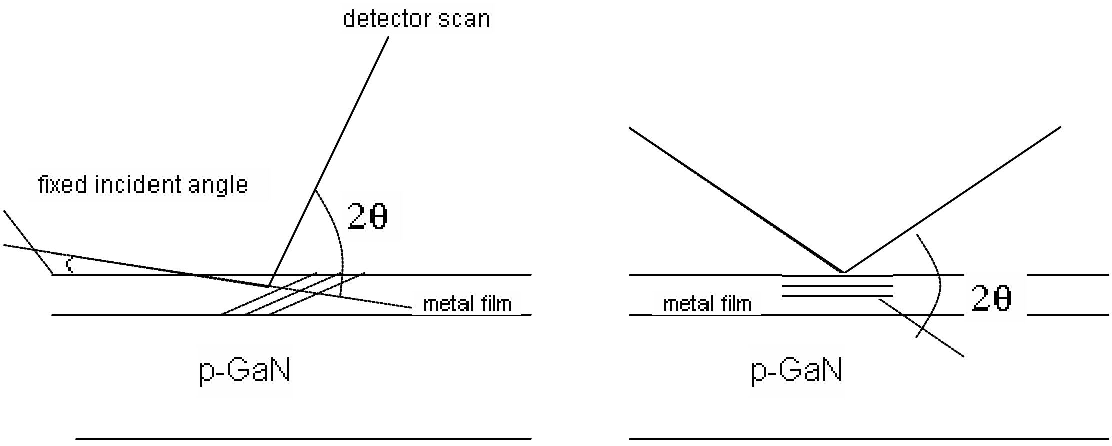


Mode A Mode B

FIG.1. Two kinds of scan modes of XRD : Mode A, scan with fixed small incident angle; Mode B, scan along the surface normal direction (ω-2θ)

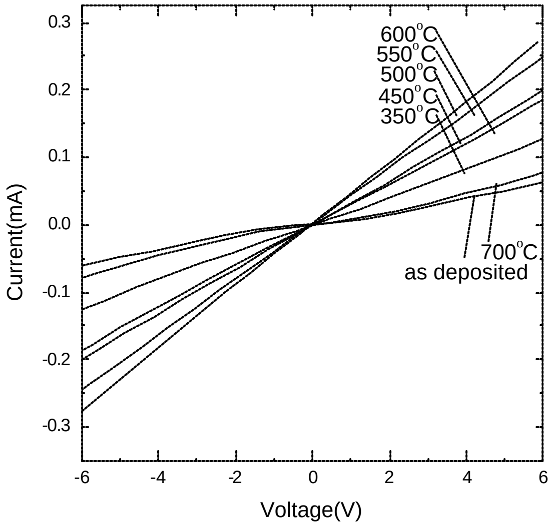


FIG. 2. The I-V curves of the Ni(20nm)/Au(20nm) contacts on p-GaN alloyed at various temperatures for 10min under air.

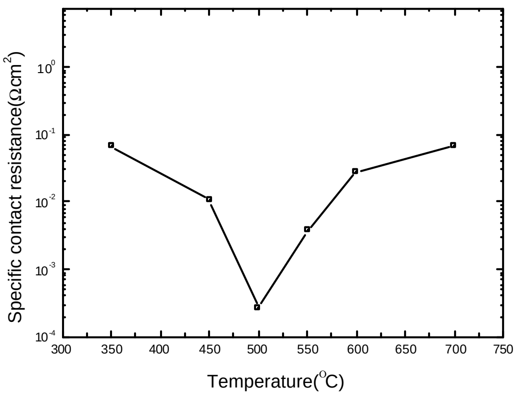


FIG.3. The effect of annealing temperature on specific contact resistance of Ni/Au contacts to p-GaN annealed in air

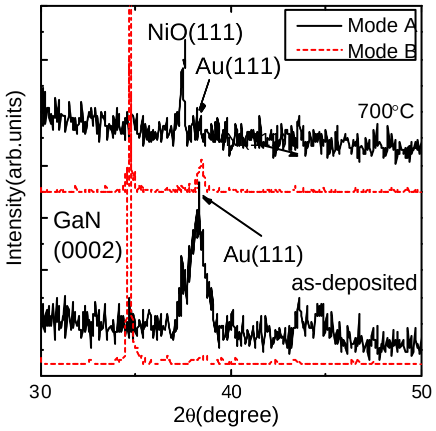


FIG. 4. Synchrotron XRD profiles of as-deposited and 700℃-annealed samples in two kinds of modes

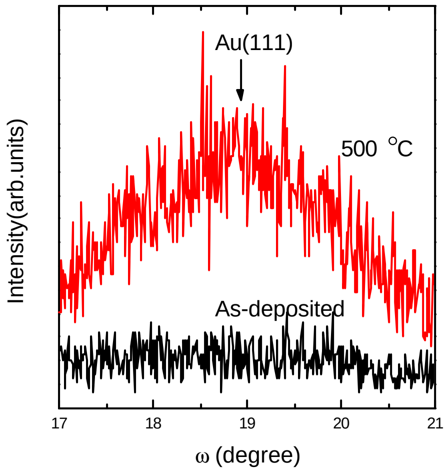
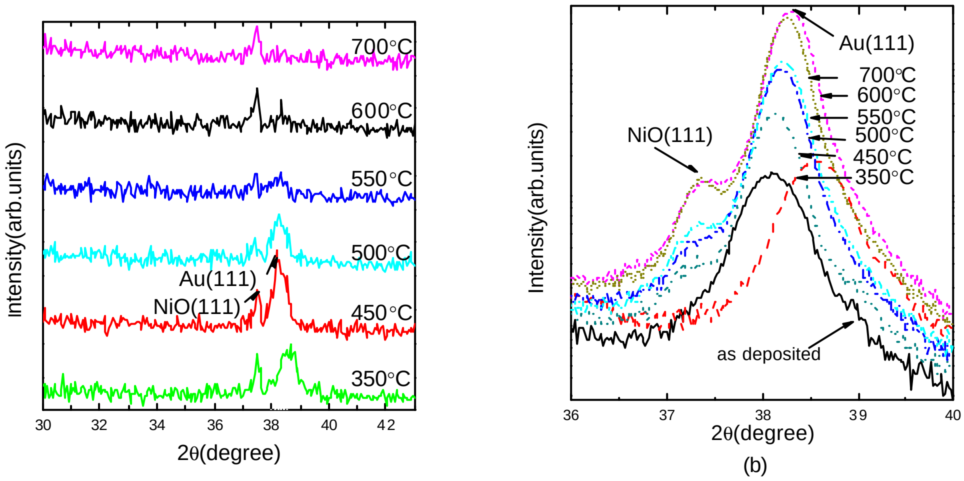


FIG. 5. Synchrotron XRD ω-scan of as-deposited and 500℃ annealed samples



(a)

(b)

FIG. 6. Microstructure evolution of Ni/Au contact to p-GaN annealed at different temperature for 10min in air ambient: (a) synchrotron XRD profiles with Mode A scan; (b) powder XRD profiles with Mode B scan.