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The Formation of p-Type ZnO Films by Thermal Diffusion from the Low Energy, High Dose Phosphorus-Implanted Si Substrate

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The p-type ZnO film is obtained out of thermal diffusion of phosphorus (P) atoms from the low energy, high dose implanted Si substrate through rapid thermal annealing (RTA). Many nonactivated P atoms exist on the surface of the shallow-implanted Si substrate and easily out-diffuse into the ZnO films at lower RTA temperatures. The concentration of the p-type ZnO reached 1.13×10^{19} cm^{-3}. The p-ZnO/n-Si heterojunction was fabricated using the one-step RTA process. This method offers various choices of dopants with low energy, high dose implanting into silicon without considering the restriction of the substrate.
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ZnO is a wide bandgap semiconductor with a potential for applications in optoelectronics, such as short-wavelength light emitting diodes and laser diodes. It has a low power pumping energy and a large exciton binding energy of 60 meV at room temperature.[1] The hexagonal wurtzite structure of ZnO films has been grown using a variety of methods, such as magnetron sputtering, pulsed laser deposition, and metallorganic chemical vapor deposition.[2-4] Obtaining a p-type ZnO layer is the important issue for realizing the ZnO-based optoelectronic devices due to self-compensation by background electron concentration (Zn interstitials and O vacancies), low solubility of dopants, and deep acceptor levels.[5,6] Recently, several groups have reported the growth of p-type ZnO by doping group-I elements of the periodic table (lithium) or group-V elements of the periodic table (nitrogen, phosphorus, arsenic, and antimony). For these acceptor dopants, phosphorus has been reported as an efficient dopant for forming a p-type ZnO layer. Kim et al. showed that phosphorus-doped ZnO thin films exhibit the reproducible p-type conduction after a rapid thermal annealing (RTA) treatment.[7] Wang et al. also presented that phosphorus-doped p-type ZnO thin films deposited on the n-Si substrate exhibited diodelike current–voltage (*I-V*) characteristics.[8] A few groups fabricated the p-type ZnO thin films by diffusing the composition of the GaAs, InP, or WN substrate.[9-11] In Ding's work, p-type ZnO thin films were created using the postannealing process, in which they deposited pure ZnO on a P-doped Si (n-Si) substrate.[12] The above-mentioned studies were constrained by the composition of the substrate or by the limited dopants concentration in the substrate. However, the composited atoms or dopants in compound semiconductors that out-diffuse into ZnO films break the bonds and escape from the matrix of the crystal during the thermal annealing process. In addition, the anomalous high p-type conductivity on the silicon substrate must be considered.[13] In their model, if the concentration of interface states is high enough for accumulating a certain negative potential at the interface, the valence band of silicon could bend above the Fermi level. Thus, an inversion layer caused by two-dimensional hole gas (2DHG) can be formed at the ZnO/Si interface. In our work, we used the high dose P-implanted silicon substrate in which the Fermi level was much closer to the conduction band due to the high enough carrier concentrations. This result can avoid the formation of 2DHG and make sure the actual conductivity in the ZnO films.

In this study, we deposited undoped ZnO thin films on a P-implanted Si(111) substrate, which was made using an ion implantation process with a high dose and a low implanting energy. Because P atoms were in high concentrations and were not activated in the surface region, they easily out-diffused into the ZnO thin films through the RTA process. A p-type ZnO layer was obtained by controlling the annealing conditions. This method is different from that using P-doped silicon and the compound semiconductor substrate in which P atoms are located at the sites of the structure matrix. In addition, the RTA method avoided the aggregation of P atoms in the surface region of ZnO films because the sample was cooled very quickly after heating stopped. The ion-implanted Si substrate became an n-type due to the P atoms being activated in the silicon crystal by the RTA process. We obtained the p-type ZnO films and fabricated the p-ZnO/n-Si heterojunction at the same time. Furthermore, it presents a thinking to select desired dopant atoms to form p-type ZnO films by using the low energy ion-implanted Si(111) as the deposited substrate.

Undoped ZnO thin films were deposited on a P-implanted silicon substrate by radio-frequency (rf) magnetron sputtering. The P-implanted silicon substrate was implanted with a dose of 1×10^{16}/cm^2 and an implanted energy of 20 keV. Its projected range is about 50 nm below the surface, and the concentration of P atoms exceeds 10^{21} cm^{-3} in the surface region.[14] The implanted Si substrates were semi-insulating before the RTA treatment. They were etched in HF (HF: D.I. H_2O = 1:9) solution for 30 s to remove the native oxide on the surface. The chamber was pumped down to 6×10^{-6} Torr before Ar and O_2 gases were introduced. The volume ratio of Ar and O_2 was controlled to be 1:1, and the working pressure was kept at 10 mTorr. The power of rf sputtering was fixed at 60 W, and the sputtering time was 40 min, yielding a layer with a thickness of 1 μm. The substrate temperature was kept at 300°C and then naturally cooled to room temperature. The samples were annealed by RTA at various temperatures (750–950°C) in 5 mTorr nitrogen gas ambient for 30 s. The Ni/Au electrodes were deposited on the ZnO layer and the Si substrate to form an ohmic contact. The crystalline microstructure of the ZnO films was studied by X-ray diffraction (XRD). The composition of these films was measured by X-ray photoelectron spectroscopy (XPS). The conduction type of the ZnO films was detected using Hall effect measurements.

The crystallization of ZnO thin films was examined by the XRD analysis; the results are shown in Fig. 1. There is a preferred orientation along the *c*-axis because only the (0002) Bragg diffraction of wurtzite ZnO appears in the XRD spectrum. In Fig. 1a, the peak position of as-deposited ZnO is 34.59°, compared to that of bulk-ZnO at 34.44°, which indicates a compressive stress in the films. The full width at half-maximum (fwhm) of 0.56° means that many defects are formed with oxygen gas ambient. Figure 1b shows the XRD pattern of p-type ZnO films after the RTA process at 850°C. The peak position is at 34.73°, which reveals that the compressive stress does not relax; it becomes larger due to the P atoms that diffused into the ZnO layer. Most of the P atoms do not substitute for the O site, but rather, a Zn antisite in ZnO:P films and form a P_{Zn}–$2V_{Zn}$ complex with a shallow acceptor level.[15] The value of

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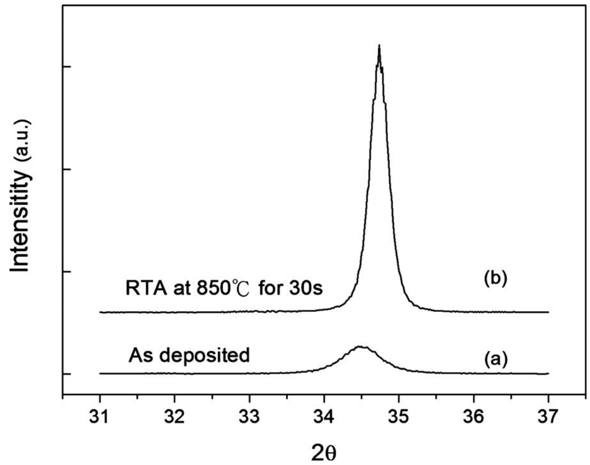

Figure 1. XRD pattern of ZnO films: (a) as-deposited and (b) RTA at 850°C for 30 s.

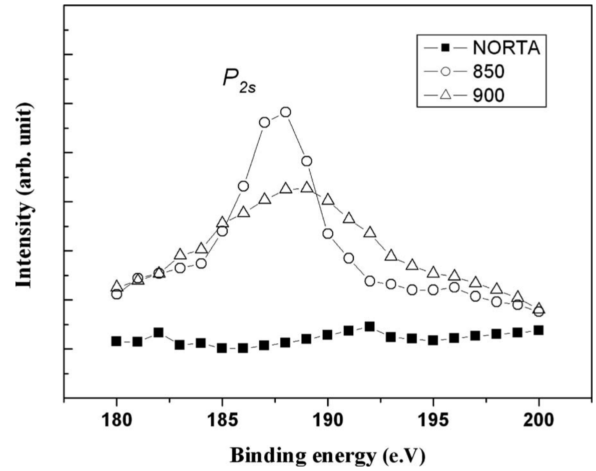

Figure 3. XPS spectra of P_{2s} core level for as-deposited ZnO films and annealing at 850 and 900°C.

fwhm was reduced to 0.268°, confirming that the annealing behavior improved the crystallization and reduced the crystal defects in the films.

To obtain the p-type ZnO films and to realize the effects of the annealing temperature on the electrical properties, the RTA temperature was varied from 750 to 950°C under nitrogen ambient at 5 mTorr. The electrical properties at various RTA temperatures were measured by Hall effect measurements. All as-grown ZnO films were semi-insulating due to the enough oxygen (O-rich) ambient. Figure 2 indicates the dependence of the carrier concentration on the RTA temperatures. The samples became conductive until the annealing temperature at 750°C and exhibited an n-type conductivity because the oxygen atoms escape from the surface of the ZnO wurtzite structure to form the level of oxygen-vacancy-related donor defects in the bandgap. At the same time, P atoms in the shallow-implanted Si layers are not activated enough at lower temperatures (750°C).[5] Until the RTA temperature was raised to 800°C, the ZnO films were inverted to p-type conductivity, and the hole concentrations reached a maximum value of 1.13×10^{19} cm^{-3} at 850°C through effective P diffusion. A proper annealing temperature is required to diffuse the P atoms from the shallow-implanted Si layer and to activate the phosphorus-related acceptors (P_{Zn}–$2V_{Zn}$ complex), which compensate O vacancies or Zn interstitials donor defects in the ZnO films.[16] Zhao et al.[13] presented that an anomalous high mobility p-type ZnO on the silicon substrate could be induced by the 2DHG at the ZnO/Si interface, in which the valence band of silicon could bend above the Fermi level; thus, an inversion layer was formed. The maximum value of the hole mobility in our samples is 2.961 cm^2 V^{-1} s^{-1}. The value of this work is lower than the reasonable maximum value of 10 cm^2 V^{-1} s^{-1}, as suggested by Look and Claflin.[17] In addition, the Fermi level could be raised by increasing the carrier concentration and is then much closer to the conduction band when the dopant concentration is high enough. For these samples with a high dose implantation, the N_D concentration was about 10^{21} cm^{-3} in the surface region.[14] Thus, the p-type conducting in our cases was not dominated by the 2DHG effect. However, the conductivity converted to n-type again when the RTA temperature exceeded 900°C. This apparent change in the electrical properties is deduced that more P atoms would diffuse into the silicon substrate, not into the ZnO films because the P solubility in the silicon was comparable to the P atom concentration at this RTA condition.[14,18] For the high dose, low energy implantation, the P concentrations in the shallow-implanted Si layer decreased with increasing annealing temperature due to dopants having a normal diffusion (in-diffusion) behavior at a higher RTA temperature (>900°C); however, the P atoms were pinned on the surface of the shallow-implanted Si layer under the lower annealing temperature (<900°C) conditions.[14,18] Therefore, there are more nonactivated P atoms to out-diffuse into ZnO films at lower annealing temperatures.

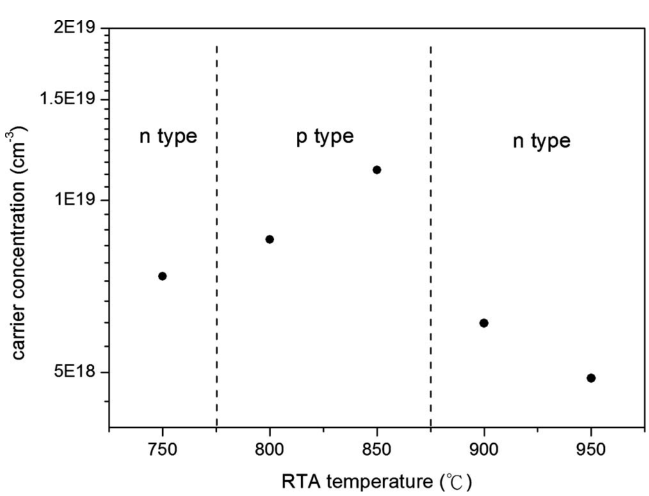

Figure 2. Room-temperature Hall effect concentration at different annealing temperatures.

The XPS results of the phosphorus bonding state in ZnO films are shown in Fig. 3a. No obvious peak related to the P_{2s} core level was found in the XPS spectrum for the film without the RTA thermal treatment,[19] indicating that the P atoms did not diffuse into the ZnO films even for the ZnO film grown at 300°C. After annealing at 850°C for 30 s, the peak of the P_{2s} core level appears, and the atomic concentration of phosphorus is 1.4%. This means that the P atoms diffuse into the ZnO films and form the P_{Zn}–$2V_{zn}$ complex, which contributes a shallow acceptor level with a lower formation energy.[16] The intensity of the P_{2s} peak decreased at 900°C, which indicates that the P concentration in ZnO films is lower than that at 850°C, and most P dopants in-diffuse into the silicon substrate deeply.

The rectification *I-V* characteristics for the p-type ZnO films on the implanted Si substrate are plotted in Fig. 4. The *I-V* curve of the Ni/Au electrode on the ZnO film is shown in the inset of Fig. 4. The linear relationship reveals that the ohmic contact characteristics are formed between the Ni/Au electrode and the p-type ZnO films. This confirms the formation of the p-n heterojunction between the n-Si (P-implanted Si) and p-type ZnO:P. The turn-on voltage is around 1

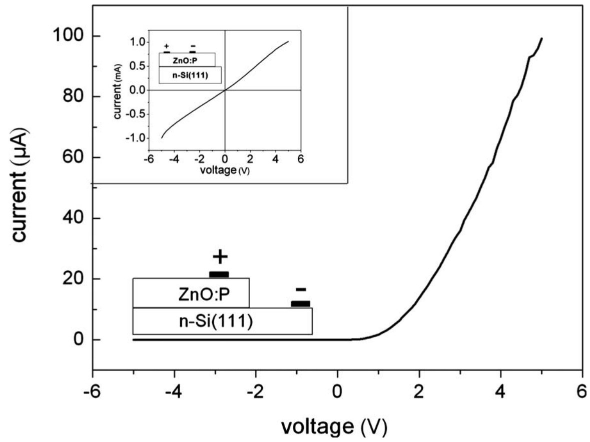

Figure 4. *I-V* characteristics of the p-ZnO/n-Si heterojunction. The inset shows the linear *I-V* characteristics of the Ni/Au electrode and the p-type ZnO layer.

V under a forward bias, and the reverse breakdown voltage is higher than 5 V. These results are similar to Wang et al.'s results.[8]

We reported a simple and quick fabrication for obtaining a p-type ZnO layer by thermal diffusion of phosphorus from a high dose, low energy implanted Si(111) substrate. Its properties were examined by XRD, XPS, and Hall effect measurements. This method allows P atoms to easily out-diffuse into ZnO films and suppresses the O vacancies at lower RTA temperatures. The conductivity type of ZnO films was controlled by the annealing temperature. The p-ZnO/n-Si heterojunction was formed using the one-step RTA process and showed the rectifying behavior. This diffusion method was not restricted by a particular substrate and combined with a popular silicon-based manufacturing process.

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