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Fabrication and evolution of nanostructure in Al_2O_3 single crystals by Zn^+ ion implantation and thermal annealing

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ABSTRACT

(0001) α-Al_2O_3 single crystals (sapphire) were implanted with Zn^+ ions at 60 keV to fluences of 1×10^{17} and 2×10^{17} ions/cm^2; and were then annealed at different temperatures under oxygen ambient. Transmission electron microscopy and optical absorption spectra were used to investigate the formation of nanostructure and their thermal evolution. Our results clearly show that the evolution of ZnO nanoparticles depends strongly on the annealing temperature and time. Zn nanoparticles could be transformed into ZnO while for annealing at a temperature 600 °C. ZnO nanoparticles were formed in the Al_2O_3 when the sample was annealed at 700 °C for 1 h. However, while annealing at 700 °C for 2 h, ZnO single-crystal film was formed on the surface of Al_2O_3. Further increasing annealing temperature to 750 °C, polycrystalline ZnO nanoclusters were formed on the surface of the sample instead of ZnO film, and leaving nanovoids band in the implanted region for the sample implanted with higher fluence. All the Zn nanoparticles disappeared and transformed to $ZnAl_2O_4$ as the annealing temperature increased to 900 °C. Photoluminescence experiment was performed at room temperature to investigate the optical properties and the quality of formed ZnO on the surface of substrate.

1. Introduction

Nanometer-size zinc-oxide (ZnO) has received scientific attention because of its promising applications in optoelectronic nanodevices [1], piezoelectric nano-generators [2], dye-sensitized solar cells [3,4], biodevices [5] and photocatalysts for degradation and complete elimination of environmental pollutants [6]. Ion implantation, as one of the most clean and flexible fabrication methods, is a powerful method to fabricate nanostructural materials because it allows reaching a high metal filling factor in substrates beyond the equilibrium limit of metal solubility and provides controllable synthesis of nanostructural materials at various depths under substrate surface. Some researchers attempted to fabrication ZnO nanoparticles (NPs) by Zn ion implantation and subsequent thermal annealing in a various substrates, including silica glass (SiO_2), CaF_2 single crystals, Al_2O_3, etc. [7–13]. Liu et al. reported that most of the ZnO NPs were formed on the surface of the SiO_2 substrate by Zn implanted silica glass combined with annealing at 700 °C in oxygen for 2 h, and sequentially in nitrogen and oxygen for 1 h [14], respectively. Amkura et al. observed the formation of ZnO NPs not only at the surface of the SiO_2 substrate but also embedded in the SiO_2 substrate when the implanted sample was annealed at 700 °C for 1 h in oxygen gas flow [15]. Xiang et al. formed ZnO NPs in the Al_2O_3 substrate after annealing in oxygen atmosphere at 600 °C [13]. In our previous work [16], we have reported the formation of ZnO films on the surface of Al_2O_3 after annealing in oxygen atmosphere at 700 °C for 2 h. Although, these earlier works have reported Zn^+ ion implantation and sequential annealing can form ZnO, states, process, and the conditions for the formation of ZnO are unclear. Since the formation and thermal evolution of ZnO NPs depends on many factors related to implantation parameters and thermal treatments conditions, a systematic investigation of the physical processes of the formation and thermal evolution of ZnO NPs is of crucial importance.

In this study, we report the formation and thermal evolution of NPs in Al_2O_3 substrates by high fluence Zn^+ ions implantation and subsequent thermal annealing. By using different analytical techniques, evolution behaviors of ZnO NPs with different annealing time and temperature in oxygen ambient have been well revealed.

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2. Experimental

Optical polished (0001) α-Al_2O_3 single crystals were implanted at room temperature by 60 keV Zn^+ ions to the fluences of 1×10^{17} and 2×10^{17} ions/cm^2 .The current density of Zn ions was less than 2 μA/cm^2 to reduce heating effects. The as-implanted samples were annealed in a tube furnace at 500 °C, 600 °C, 700 °C, 800 °C and 900 °C for 1 h, and 700 °C, 750 °C for 2 h under flowing oxygen gas. The microstructure of the annealed samples was investigated by using a JEOL JEM 2010 (HT) operated at 200 kV. Cross-sectional transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were used for determining the crystal structure. After ion implantation and annealing, the optical absorption spectra were recorded at room temperature using a UV–VIS–NIR dual-beam spectrophotometer (Varian Cary 5000) with wavelengths varying from 200 to 800 nm. The photoluminescence (PL) was excited at room temperature by a 325 nm line of He–Cd laser.

3. Results and discussion

Fig. 1 shows the optical absorption spectra of the Al_2O_3 samples implanted with 60 keV Zn^+ ions to the fluence of 1×10^{17} and 2×10^{17} ions/cm^2 and the corresponding annealed samples in oxygen ambient at different temperatures for 1 h. Strong and broad absorption peaks at about 290 nm appear in the as-implanted sample. The absorption peaks are attributed to the surface plasmon resonance (SPR) absorption of Zn NPs [17]. After annealing at 500 °C, it can be seen that the intensity of the SPR peaks decrease greatly while their positions shift slightly toward the longer wavelength. There are two possible reasons that cause the peak shift. One is that Zn NPs were oxidized during the annealing process. Another one is due to the growth of Zn NPs with the increase of annealing temperature [18]. As the annealing temperature increased to 600 °C, the Zn SPR absorption peak disappears and a new absorption edge around 370 nm appears which relates to the exciton absorption of ZnO [19]. As the annealing temperature reached to 700 °C, the spectrum only shows the weak SPR edge of ZnO. Further increasing annealing temperature to 900 °C for the sample with implanted with 2×10^{17} ions/cm^2, the SPR absorption edge of ZnO disappears because when the sample was annealed in oxygen ambient at a higher temperature of 900 °C, the solid-phase diffusion reaction between the implanted Zn and Al_2O_3 matrix yields the formation of $ZnAl_2O_4$ [20].

In order to study the effect of the annealing time on the evolution of formed ZnO, we prolonged annealing time to 2 h at 700 °C and 750 °C. ZnO exciton absorption edge is observed in all the annealed samples as shown in Fig. 2, which indicates that the ZnO has been formed.

From the optical absorption spectra of the annealed samples, it is obvious that ZnO was formed by annealing in oxygen ambient from 600 °C to 800 °C. However, the further knowledge about the state of formed ZnO (NPs or film, embedded in the substrate or on the surface of the substrate) after annealing is unclear. In order to reveal the thermal evolution of ZnO, the cross-sectional TEM images and corresponding SAED patterns of Zn^+ implanted sample with fluence of 1×10^{17} ions/cm^2 annealed at 700 °C for 1 h (a), 2 h (b), 750 °C for 2 h (c), and 2×10^{17} ions/cm^2 at 750 °C for 2 h (d) are presented in Fig. 3. Fig. 3(a) clearly shows that nearly spherical-shape ZnO NPs were formed near the surface of the Al_2O_3 substrate. The SAED pattern in Fig. 3(b) shows that a single-crystal ZnO film was formed on the surface of the Al_2O_3. By comparing Fig. 3(b) and (c), it is observed that the morphology of formed ZnO

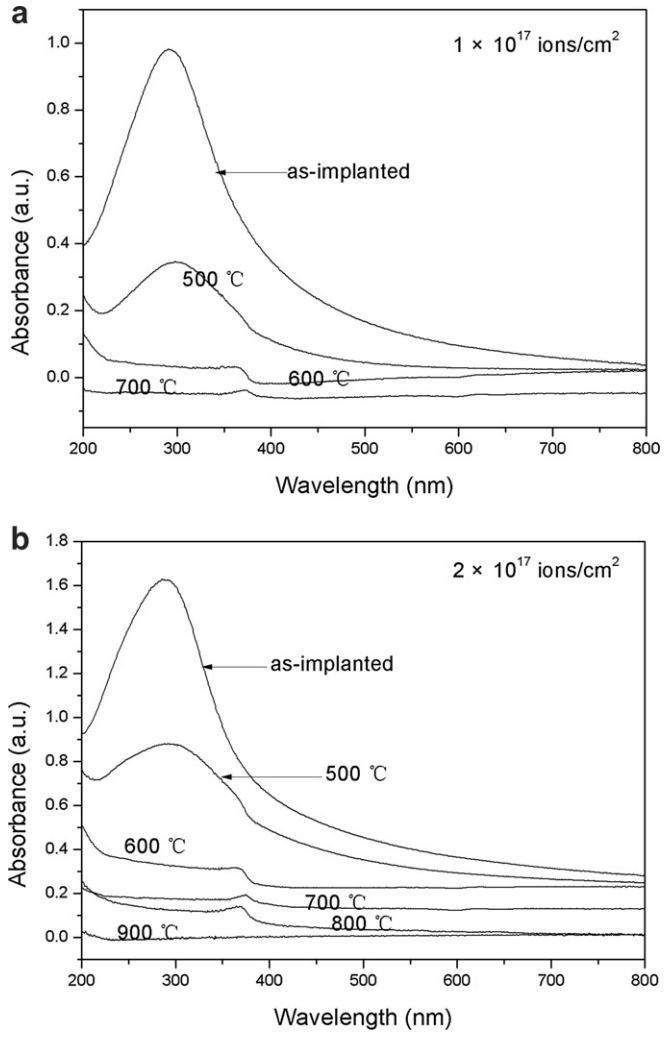

Fig. 1. Optical absorption spectra of the as-implanted and annealed samples at different temperatures with the fluence of (a) 1×10^{17} ions/cm^2, (b) 2×10^{17} ions/cm^2.

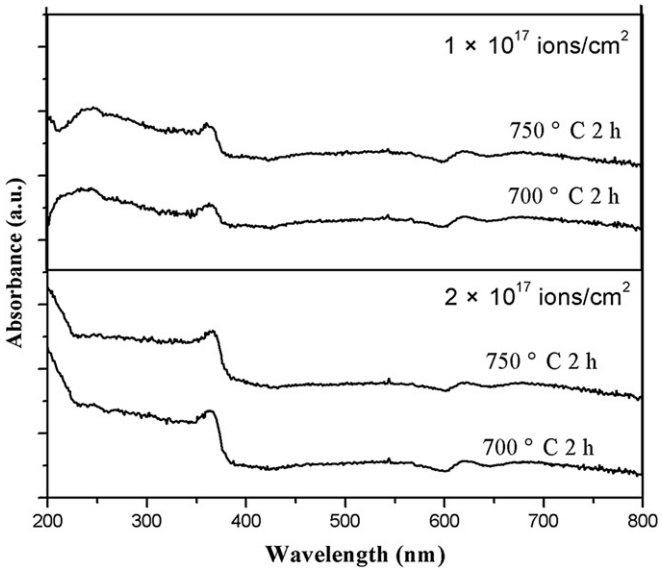

Fig. 2. Optical absorption spectra of the implanted samples annealed at 700 °C and 750 °C for 2 h with the fluences of 1×10^{17} and 2×10^{17} ions/cm^2.