Luminescence of SiO₂ Film Implanted with Ge Negative Ions

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The cathodeluminescences (CL), photoluminescence (PL), and electroluminescence (EL) properties of Ge implanted SiO₂ films (SiO₂:Ge) were investigated. The SiO₂ films on Si substrate were implanted with Ge-negative ions. The implanted Ge atom concentrations in the films were 3 and 6 at. %. Ge nanoparticles were formed in the SiO₂ films after annealing. CL, PL and EL were observed at wavelengths around 400 nm from the SiO₂:Ge films. CL of GeO₂ films were also investigated. The CL intensity from the GeO₂ films is obviously lower than that from the SiO₂:Ge films with 6 at.% of Ge atomic concentration. Strong EL from large area of the films was not only to be easily seen with naked eye but also to be measured its wavelength. Operating voltage was an order of magnitude lower and the emitting area was two orders of larger than those reported previously. These results suggested that annealing of SiO₂:Ge films in moderate oxidative atmosphere is suitable method for the strong luminescence due to Ge-related oxygen deficient center (Ge-ODC).

Key words: Nanoparticles, Ion implantation, Oxide film, Germanium Negative ion, Luminescence

1. INTRODUCTION

A Semiconductor is attractive materials for light-emitting devices. Especially semiconductor materials compatible with the standard Si technology are desired for the development of light emission source for communication in a LSI chip. For example, silicon and germanium in silicon-dioxide layers are expected to apply to electroluminescence source in LSI chips, since 500-nm-thick SiO₂ films implanted with Ge⁺ ions were reported to show blue and violet electroluminescence by applying a voltage of 350 V [1]. However, it is not only required to decrease the operation voltage [2] but also required to increase the luminescence intensity for various application. In order to meet this requirement, we have tried to implant Ge ions into a shallow region in SiO₂ layer on Si substrate by using a negative-ion implantation method with multi-energy. Moreover, we studied the cathodeluminescence (CL) of thermally grown GeO₂ films and of Ge implanted SiO₂ films (SiO₂:Ge). Negative-ion implantation has an advantage of almost "charge-up free" feature for insulators [3]. Therefore, the penetration depth of ions can be controlled correctly with a relatively low energy implantation into a thin insulator such as silicon dioxide. Moreover, the technique is suitable for careful examination about implanted atoms in thin dielectric films such as SiO₂ films, because the charge up can make accidental dispersion of implanted atoms and can cause break down of dielectric films to make accidental defects in the films.

2. EXPERIMENTAL

Germanium negative ions (Ge⁻) were implanted at room temperature into SiO₂ films with thickness of 100

and 50 nm thermally grown on Silicon substrate (Shin-Etsu Chemical Co., Ltd.). We used a multi-energy implantation technique to make a regions of the SiO₂:Ge films. In the multi-energy implantation, the Ge⁻ were implanted three times into the same sample by changing the energies of 50, 20 and 10 keV. Maximum Ge atom concentrations in the SiO₂:Ge films were ranging from 3 or 6 at.%. For example, the concentration profiles for Ge atoms about 3 at.% at peak concentration is shown in Fig. 1. The profiles were calculated by using the Transport of Ions in Matter (TRIM-DYN) program [4].

Fig. 1. Depth profile of Ge atoms implanted into SiO₂ medium calculated by using TRIM-DYN program under conditions of multi-energy implanted at 50 keV with 7.0×10^{15} , 20 keV with 1.6×10^{15} and 10 keV with 1.1×10^{15} ions/cm².

Fig. 2. Optical reflectance spectra for Germanium substrate before and after thermal annealing in O₂ atmosphere.

The total concentration curve in Fig. 1 expects the formation of a layer with Ge concentration of about 3 at.% from 10 nm to 40 nm in depth. The gas pressure during the implantation was kept less than 1×10^{-4} Pa. We expected to obtain SiO₂:Ge films with about 30-nm-thick Ge implanted region by the multi-energy implantation. The Ge implanted SiO₂:Ge films were then annealed at 800 °C for 1 h by an electrical oven in a quartz tube with a N₂ gas flow (50 ml/min) under low vacuum condition by a rotary pump (400 l/min).

The GeO₂ films were grown by oxidation of Ge substrates (Furuuchi chemical Co., Ltd., Japan) at 550°C for 3 h in O₂ gas flow. A GeO₂ films with thickness of about 100 nm were formed on the Ge substrates. Fig. 2 shows reflectance spectra obtained from the Ge substrate before and after thermal oxidation. The reflectance is obviously decreased after thermal oxidation. The reduction of reflectance indicates that germanium atoms near the surface were oxidized.

CL of the SiO₂:Ge and GeO₂:Ge films were investigated with using an electron beam at 5 keV.

PL and EL of the SiO₂:Ge films were investigated in RF-5300PC Shimadzu spectrometer with a R955 Hamamatsu photomultiplier. For PL observation, 150W Xenon lamp within the spectrometer was used as a

Fig. 4. CL spectra of Ge implanted SiO₂:Ge film in comparison to unimplanted SiO₂ film.

source of 240 nm excitation light. For EL observation, metal-oxide-semiconductor (MOS) device structures as shown in Fig. 3, were prepared by sputtering indium tin oxide (ITO) as front side electrode and evaporating Al as rear side electrode.

Cross-sectional TEM images were obtained using a scanning-type TEM of EM-002B (Topcon Techno), operating at 200keV.

3. RESULTS AND DISCUSSION

Cathodeluminescence (CL) of the SiO₂:Ge films with 6 at.% implanted Ge peak concentration after annealing at 800°C in N₂ for 1 h were investigated. Fig. 4 shows CL spectra of the Ge implanted SiO₂:Ge film and from an unimplanted SiO₂ film at room temperature measurement. The unimplanted SiO₂ film showed only broad luminescence peak at around 460 nm, but the Ge implanted SiO₂:Ge film showed large sharp luminescence peak at around 400 nm. This luminescence peak is well agreed with the CL spectra reported by Rebohle et al [1] and H. J. Fitting et al [5]. Therefore, the peak around 400 nm is considered to be due to oxygen deficient center (ODC) attributing to two fold-coordinate Ge atoms.

Fig. 3. A schematic view of light emitting devices with simple MOS structure.

Fig. 5. CL spectra of thermally grown GeO₂ film in comparison to Ge substrate before thermal annealing.

Fig. 6. PL and EL spectra of $\text{SiO}_2\text{:Ge}$ films with 3 at.% implanted Ge peak concentration after annealing at 700°C in Air for 2 h.

Fig. 5 shows CL spectra of the thermally grown GeO_2 films on Ge substrate and from the Ge substrate before oxidation at room temperature measurement. The Ge substrate before oxidation could scarcely show luminescence between 250 and 500 nm, but the GeO_2 film showed weak luminescence peak at around 400 nm. These luminescence peaks seem corresponding to above CL peak in Fig. 4. Although total amounts of mono-oxidized Ge atoms and di-oxidized Ge atoms in the thermally grown GeO_2 films were much more than those in the Ge implanted $\text{SiO}_2\text{:Ge}$ films, the intensity of luminescence from the GeO_2 films was obviously not more than that from the Ge implanted $\text{SiO}_2\text{:Ge}$ films. CL intensity from the $\text{GeO}_2\text{:Ge}$ films was a order of magnitude lower than that from $\text{SiO}_2\text{:Ge}$ films with only 6 at.% of Ge atom concentration after annealing.

These results suggested that the strong luminescence could be generated by tuning condition of Ge implantation and subsequence annealing.

PL and EL of the $\text{SiO}_2\text{:Ge}$ films with 3 at.% implanted Ge peak concentration after annealing at 700°C in low pressure air for 2 h were investigated at room temperature. For EL measurement the ITO electrode of about 10 mm square was much larger than that of about 1 mm in diameter in previous work by other groups [1], and was enough large for Ge implanted area of 8 mm in diameter. Strongly emitted luminescence was expected due to forming much GeO by moderate oxidation of Ge. At applying 1kHz-AC voltage of about 35 V, strong EL from large area were not only to be easily seen with naked eye but also to be measured its wavelength by RF-5300PC Shimadzu spectrometer. Fig. 6 shows EL and PL spectra of the Ge implanted $\text{SiO}_2\text{:Ge}$ film at 3 at.% after annealing at 700°C at room temperature measurement. The Ge implanted $\text{SiO}_2\text{:Ge}$ film showed large luminescence peak at around 400 nm for EL as well as PL. This EL spectra measured in wavelength of 350 to 500 nm is well agreed with the PL spectra. Luminescence peak at around 300 nm was shown in PL but not in EL. This disappearance in EL may be due to ITO which is opaque for light in shorter wavelength than around 300 nm. These luminescence spectra were well agreed with spectra reported by Rebohle et al [1], and

Fig. 7. Cross-sectional TEM images of $\text{SiO}_2\text{:Ge}$ films with 3 at.% implanted Ge peak concentration after annealing at 700°C in Air for 2 h.

moreover, the operating voltage was an order of magnitude lower and the emitting area was two orders of larger than those reported by them.

These improvements would be realized by relatively long time annealing at suitable temperature for Ge nanoparticle-formation as well as in suitable oxidative atmosphere for GeO -formation.

The TEM images of the films are shown in Fig. 7. Ge nanoparticles with 2-3 nm in diameter were formed in the middle of the film at 11-37 nm in depth.

The Ge nanoparticles were formed with gathering Ge atoms implanted in the films. Some surplus Ge atoms in the films could form leak passes like ion irradiated defects and could not contribute light emission. The suitable annealing reduced the surplus Ge atoms and irradiated defects in the films so that the films were of greater stability than those in the previous reports [1]. In the previous report, the Ge implanted $\text{SiO}_2\text{:Ge}$ films were annealed at relatively high temperature around 1000°C for relatively short time in a inert gas.

These results suggested that the strong luminescence was generated due to oxidation of Ge nanoparticles in the $\text{SiO}_2\text{:Ge}$ films. It might indicate that not only Ge-oxidation but also Ge nanoparticles-formation was important for strong light emission source with Ge-ODC. Nanoparticles might be suitable for generation and/or stabilization of the ODC.

4. CONCLUSION

Flat profiles of Ge atom concentration in some regions of SiO_2 films can be formed by using a multi-energy implantation technique. In the multi-energy implantation, Ge^+ ions were implanted three times into the same SiO_2 films by changing the energies of 50, 20 and 10 keV. The CL spectra of the Ge implanted $\text{SiO}_2\text{:Ge}$ films showed peaks around 400 nm in wavelength. We also studied the thermally grown GeO_2 films. Although it showed luminescence peak corresponding to the same position peak from the Ge implanted $\text{SiO}_2\text{:Ge}$ films, the intensity of luminescence from the thermally grown GeO_2 films was obviously weaker than that from the Ge implanted $\text{SiO}_2\text{:Ge}$ films. The $\text{SiO}_2\text{:Ge}$ films with 3 at.% implanted Ge peak concentration after annealing at 700°C in low pressure air for 2 h showed large

luminescence peak at around 400 nm for EL as well as PL. The operating voltage was lower and the emitting area was larger than those ever reported. This improvement might be realized by the annealing in moderate oxidative atmosphere. These results might provide guidance in strong light emission in UV-blue region from SiO₂:Ge films.

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