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NANOSTRUCTURE AND PHOTOLUMINESCENCE PROPERTY OF Si/MgO AND Si/ZnO CO-SPUTTERED FILMS

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Abstract *— Si/MgO and Si/ZnO films were deposited by placing Si plates on an MgO or ZnO target during sputter deposition. X-ray photoelectron spectroscopic (XPS) analysis revealed that the average Si valency was 3.1 for Si/MgO and 2.6 for Si/ZnO co-sputtered films when Si contents were 20%. Diffraction peaks of not Si-derived but less crystallized matrix were observed at low Si content ranges. Both films are seen to have structures with nanoparticle dispersion from TEM observation. The PL emission observed at 1.7 eV for Si/MgO and at 2.0 eV for Si/ZnO is deduced to arise from the electron-hole recombination mechanism in SiO_x at the interface, which is similar to the Si/SiO_2 co-sputtered film.* ©*1999 Acta Metallurgica Inc.*

INTRODUCTION

Nano-sized silicons, such as porous silicon and silicon nanoparticles, have attracted much scientific attention because of their photoluminescence (PL) properties (1,2). Si/SiO_2 nanocomposites prepared by co-sputtering and heat treatment have structures embedded with nano-sized silicon (3-6). The photoluminescence of Si nanostructures is considered to originate from the quantum confinement effect of Si nanoparticles and/or the luminescence center at the Si/SiO_2 interface, but the mechanism is still controversial. In order to pursue the possibility of obtaining Si nanoparticles embedded in different matrix materials other than SiO_2, we deposited thin films by sputtering an Al_2O_3, MgO, TiO_2 or ZnO target on which the Si plates are placed (7,8). In this paper, we focus on Si/MgO and Si/ZnO co-sputtered films because these two have interesting nanostructures and PL properties. The correlations between structure, the chemical state of silicon and the PL property of these films are discussed.

EXPERIMENTAL

Co-sputtered films of Si/MgO and Si/ZnO were prepared on SiO_2 substrates using an r.f. sputtering apparatus (Shimadzu HSR-521). Si plates (Osaka Titanium Co. Ltd., n-type) were

symmetrically placed on an MgO or ZnO target 100 mm in diameter for co-sputtering. In order to study the effect of Si addition in small amounts in this paper, the size of the Si plates used was 5 mm × 5 mm, which was a third of the plate size used in the previous experiments (7,8). Thus the content of Si in the films was small even though the number of Si plates were the same as before. The sputtering power, atmosphere and deposition time for Si/MgO and Si/ZnO were 200 W, 0.53 Pa of Ar for 90 min and 100 W, 1.3 Pa of Ar for 60 min, respectively. The thicknesses of the films were approximately 500 nm and 800 nm. Throughout this paper, notations like Si(12)/MgO are used, where the number in parentheses is the number of Si plates placed on the target. Heat treatment was performed for 3 h in a vacuum. The equipment used for characterization and PL measurement was the same as that used in the previous experiments (7,8).

RESULTS AND DISCUSSION

Figure 1 shows the change in Si content of as-deposited Si/MgO and Si/ZnO films with the increase in the number of Si plates which were analyzed by XPS. The content of both films almost linearly increased with the use of up to 12 Si plates, where the atomic concentration of Si was about 20%. Diffusion and reaction of the components occurred by heat treatment above 500 °C for Si/MgO and 600 °C for Si/ZnO in the high Si concentration range. For Si/MgO, the Si component migrated into the interior of the film, resulting in the formation of an MgO layer at the surface. In contrast, the Si component was enriched at the surface for Si/ZnO co-sputtered film.

Figure 2 shows the Si2p XPS spectra of Si(12)/MgO and Si(12)/ZnO co-sputtered films annealed at 400 °C. The same procedure as that described in the previous paper (7) was applied to analyze these data. First, the charge-up shifts of the peaks were calibrated by taking the Mg2p peak from MgO to be 50.8 eV and the Zn2p peak from ZnO to be 1021.8 eV (9). A small metallic Mg peak at 49.0 eV was observed in the Si/MgO film, indicating that Si in a low valency state reduced a small amount of MgO. There was only one component of ZnO in the Zn2p peak from Si/ZnO film. Second, curve fitting calculations were performed for these Si2p peaks, assuming the existence of the following five components: Si metal, Si^{+}, Si^{2+}, Si^{3+}, Si^{4+}, and the binding

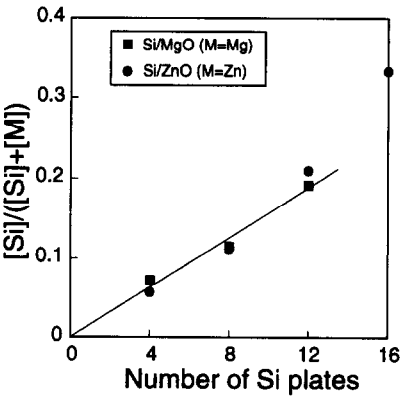

Fig. 1 Changes in Si contents of as-deposited Si/MgO and Si/ZnO co-sputtered films analyzed by XPS.

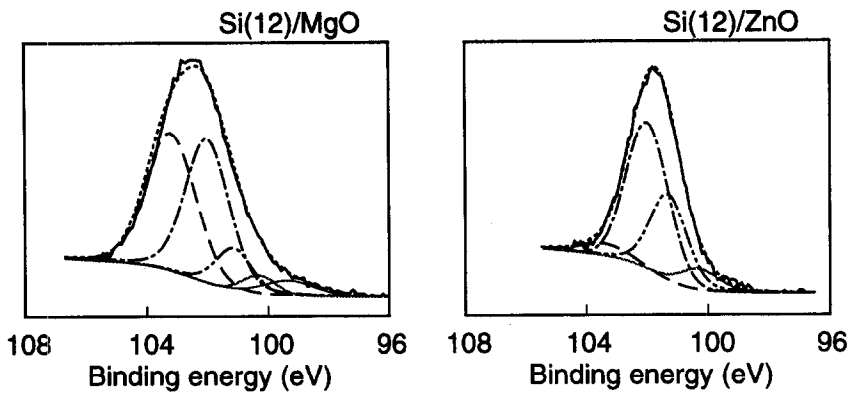

Fig. 2 Si2p XPS spectra of Si(12)/MgO and Si(12)/ZnO co-sputtered films annealed at 400 °C with the results of curve fitting calculations. The band at about 102.3 eV is the Si^{3+} component.

energies and FWHMs of these components. The results of the curve fitting calculations are also shown in Fig. 2. Tri- and tetra- valent silicon was the main component for Si/MgO film, and the tri-valent state was dominant in Si/ZnO film. The average valence of Si/MgO and Si/ZnO was 3.1 and 2.6, respectively.

In the Si(12)/MgO film, a weak and broad MgO(200) peak and no Si-derived peak were observed in the XRD spectra, though a sputtered MgO film showed a strong (200) peak. The shape of the MgO(200) peak did not greatly change even through heat treatment at 900 °C. In the Si/ZnO film, the films sputtered with 4 or 8 Si plates on a ZnO target showed a small and broad ZnO(002) peak, which became sharp by annealing at 600 °C. However, for Si(12)/ZnO film, heat treatment at 400 to 600 °C was required to obtain ZnO(002) orientation. Both Si(12)/MgO and Si(12)/ZnO films are seen to have structures with nanoparticle dispersion from TEM observation.

The PL spectra of MgO and Si(12)/MgO sputtered films are shown in Fig. 3. MgO is known to show PL at 2.0 eV (10). Si(12)/MgO, however, showed stronger PL at 1.8 eV than

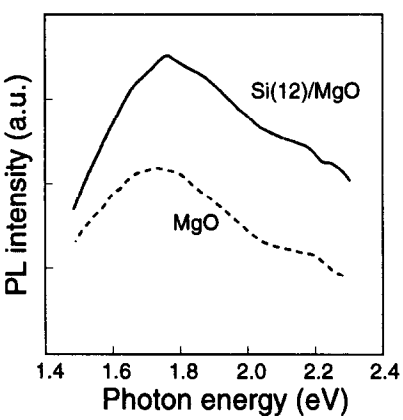

Fig. 3 Photoluminescence spectra of MgO and Si(12)/MgO sputtered films measured at 300K.

MgO as shown in Fig. 3. In our previous paper (7), we studied the relationship of PL and the Si2p XPS spectra of the Si/SiO_2, Si/Al_2O_3 and Si/MgO co-sputtered films, and concluded that the SiO_x ($0<x<2$) content calculated from the XPS spectra is important for the PL emission at 1.7 eV (730 nm) observed in Si/SiO_2 co-sputtered films, because it is thought to be due to the recombination of electrons and holes in the SiO_x region at the interface. In the previous analysis (7), Si/MgO co-sputtered films (Si content: 28%) had quite small PL intensities, because the proportion of the SiO_x component was only about 20% of all Si components, even though the concentration of the metallic Si component was as high as 23%. The 1.7 eV emission was, however, observed through a similar mechanism in this experiment, probably because the proportion of the SiO_x component was high enough at 54%. In contrast, Si(8)/ZnO co-sputtered film annealed at 400 °C had ZnO(002) orientation and similar XPS spectra, and showed PL peaked at about 2.0 eV (610 nm). Although the energy of this PL is slightly large, it can be ascribed to the electron-hole recombination process in SiO_x (11).

SUMMARY

The nanostructure and photoluminescence of Si/MgO and Si/ZnO co-sputtered films, whose Si contents were about 20% were studied. From the XPS analysis, the principal low valency Si state was Si^{3+} for Si/MgO and Si/ZnO at this Si content range. These films had nanocomposite structures. PL emissions at 1.7 eV for Si/MgO and at 2.0eV for Si/ZnO were observed. They can be ascribed to the electron-hole recombination process in SiO_x at the interface.

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