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Effect of film thickness on electrical property of microcrystalline silicon

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Abstract

We report dependences of electrical properties on SiH_4/H_2 dilution rate and film thickness for microcrystalline silicon films formed by a hydrogen radical-induced chemical vapor deposition (HRCVD) method. The electrical conductivity of the films at SiH_4 18 sccm /H_2 120 sccm was markedly increased to 10^{-3} S/cm as film thickness increased above 100 nm. Crystalline grains with (2 2 0) orientation were formed. Theoretical analysis revealed that grain boundaries among (2 2 0) grains had a low defect density of $1 \times 10^{12}\,cm^{-2}$ so that the high conductivity was achieved.

Keywords: Microcrystalline silicon; HRCVD; Electrical conductivity

1. Introduction

Microcrystalline silicon films are in general, the mixture structure of amorphous phase and crystalline phase. The structure is very complex. For example, a region near glass substrate can be amorphous. Thick film formation requires to achieve a high crystalline volume ratio [1].

In this paper, we demonstrate that crystalline orientation depends on SiH_4/H_2 dilution ratio for hydrogen radical-induced CVD. We also report an analysis of a low defect density between (2 2 0)-oriented grains resulting in a high electrical conductivity.

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2. Experimental details

Microcrystalline silicon films were formed on glass substrates using a hydrogen radical-induced chemical vapor deposition (HRCVD) method, in which SiH_4 gas was decomposed by hydrogen radicals supplied through 2.45 GHz microwave discharge (40 W) of H_2 gas at the quartz tube [2,3]. Microcrystalline silicon films were formed at 200°C and 250°C. H_2 gas flow rate was 120 sccm. SiH_4 gas flow rate was varied from 6 to 18 sccm. The total gas pressure at film deposition was 0.4 Torr.

The electrical conductivity of microcrystalline silicon films was measured with Al coplanar electrode at room temperature. The photoconductivity of the films was measured under AM-1.5 illumination (100 mW/cm^2). The Al electrodes with a gap of 20 μm and width of 2000 μm were formed on the microcrystalline silicon films by photolithography and wet-etching process. A bias voltage of 5 V was applied.

Crystalline properties were investigated by X-ray diffraction (XRD) at room temperature. The wavelength of X-ray (Cu K_α) was 1.542 Å. Circular islands of silicon films with a diameter of about 7 mm were defined at the middle of the substrates using photolithography and dry-etching process in order to measure the XRD spectra of only the middle region of samples.

Crystalline properties were also estimated from measurements of optical reflectivity spectra in ultraviolet wavelength regions. Crystalline silicon has a peak around 276 nm (E_2 peak) in optical reflectivity spectra, which is caused by large joint density of states at the X point in Brillouin zone, while amorphous silicon has no peak around 276 nm. Because the optical absorption coefficient is large $\sim 10^6\,\mathrm{cm}^{-1}$ in the ultraviolet region, crystalline states at surface regions can be investigated with 10 nm resolution in the depth direction.

3. Results and discussions

Fig. 1 shows that the dark and photo-electrical conductivity of silicon films formed at 250°C as a function of film thickness with SiH_4 flow rates of 6 (a) and 18 sccm (b) under 120 sccm H_2 gas flow. The dark electrical conductivity was low 10^{-6}–10^{-7} S/cm for SiH_4 flow rate of 6 sccm case and photo conductivity was also very low – 10^{-6} S/cm. On the other hand, the electrical conductivity markedly increased from 10^{-6} to 10^{-3} S/cm for the SiH_4 flow rate of 18 sccm when film thickness was above 150 nm as photo-electrical conductivity was also larger by 1–2 orders of magnitude than dark electrical conductivity as shown in Fig. 1.

Fig. 2 shows that crystalline volume ratio obtained from E_2 peak of microcrystalline silicon films as a function of film thickness. Crystalline volume ratio of the silicon film formed at SiH_4 flow rate of 6 sccm increased from 0.22 to 0.35 as film thickness increased from 50 nm to 250 nm, although the electrical conductivity was low and almost independent of film thickness. On the other hand, crystalline volume ratio of the silicon films formed at SiH_4 flow rate of 18 sccm was low at ~ 0.17, independent of film thickness. This means that crystalline volume ratio was almost same for any film thickness. However, the increase in the electrical conductivity suggests that

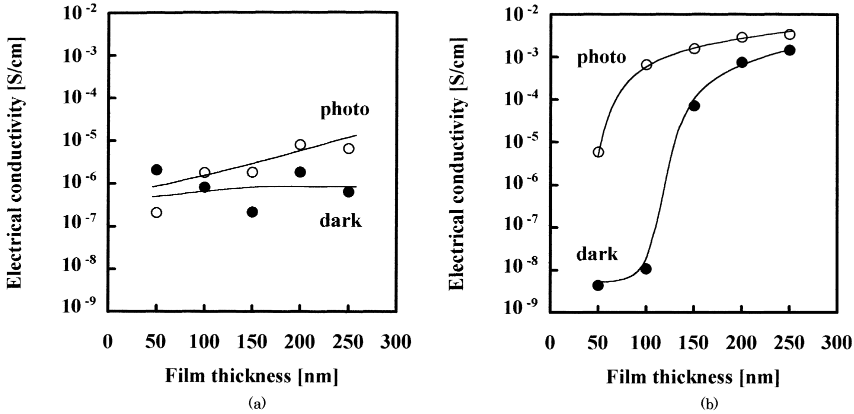

Fig. 1. The electrical conductivity (photo and dark) as a function of the film thickness of the microcrystalline silicon films formed at low SiH_4 flow rate of 6 sccm (a) and high SiH_4 flow rate of 18 sccm (b).

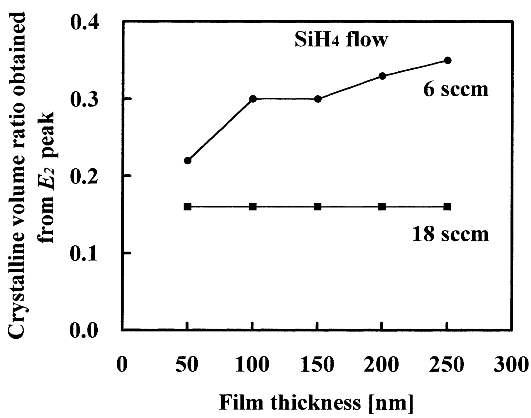

Fig. 2. The crystalline volume ratio as a function of film thickness of the microcrystalline silicon films formed at SiH_4 flow rate of 6 and 18 sccm.

carrier density increased as film thickness increased. Fig. 3 shows that X-ray diffraction spectra of the silicon films formed at SiH_4 flow rate of 6 and 18 sccm. The preferential crystalline orientation was (1 1 1) at low SiH_4 gas flow rate of 6 sccm and (2 2 0) at high flow rate of 18 sccm.

We analyzed the electrical conductivity for films with different preferential crystalline orientations using statistical thermodynamical condition between free carriers, dopant atoms and defect state. We assumed that oxygen atoms intentionally were incorporated into films during film deposition and donor state at 0.18 eV below conduction band edge [4].

We analyzed the change in the electrical conductivity of microcrystalline films using a statistical analysis program. We introduced an accepter-type defect states at the

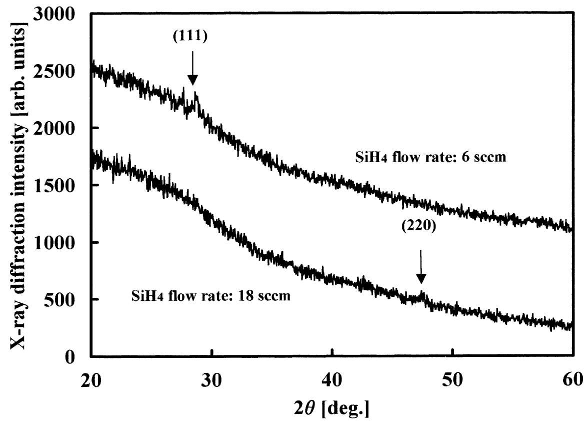

Fig. 3. X-ray diffraction spectra of the silicon films formed at SiH_4 flow rate of 6 and 18 sccm.

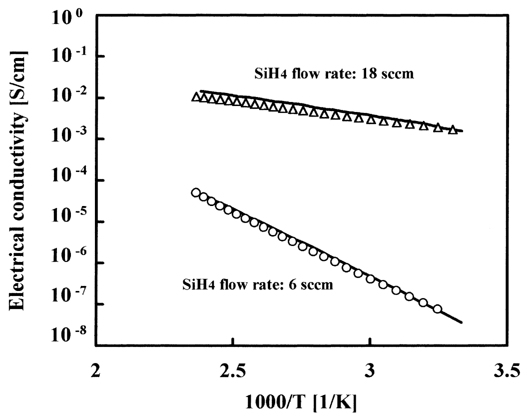

Fig. 4. The calculated (solid curves) and experimental (dotted curves) conductivity as a reciprocal function of absolute temperature ($1/T$).

mid-gap at grain boundaries. Oxygen dopant atoms were assumed to be distributed uniformly in silicon films with an energy level 0.18 eV below the conduction band edge. Electron carriers are generated from the dopant atoms via their ionization, whose probability is determined with the Fermi–Dirac statistical distribution function. Free carriers are trapped by the localized defect states and defects are charged negatively. The Fermi energy level is determined by the statistical thremodynamical conditions keeping the charge neutrally among the densities ionized dopant atoms (N_d), defect states charged negatively with electron carriers (X_d) and free carriers (n), $N_d = n + X_d$, in the whole region including crystalline grains and grain boundaries. However, the density of ionized donors is larger than that of free electron in crystalline grains because some electrons produced from intentionally doped oxygen atoms are trapped at grain boundaries. This space-charge effect in crystalline grains causes the band bending and results in the potential barrier at grain boundaries.

Agreement between temperature dependencies of calculated and experimental conductivities shown in Fig. 4 revealed that planes of grain boundaries had a defect density at $1\times10^{12}\,cm^{-2}$ for films (2 2 0) orientated. On the other hand, the defect density was $2.15\times10^{12}\,cm^{-2}$ for films (1 1 1) oriented. The high defect density resulted in the low dark and photo-electrical conductivity because of trapping carriers, as shown in Figs. 2 and 3.

4. Conclusions

We prepared microcrystalline silicon films using HRCVD method for different SiH_4/H_2 dilution ratio and film thickness. The electrical conductivity of microcrystalline silicon films was markedly depended on the film thickness at high SiH_4/H_2 dilution ratio of 18/120 sccm. The crystalline orientation for SiH_4/H_2 dilution ratio of 18/120 was (2 2 0). In crystalline orientation (2 2 0), low defect density of $1\times10^{12}\,cm^{-2}$ compared with the case of (1 1 1) orientation at grain boundaries would bring out high conductivity.

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