大気圧マイクロプラズマジェットの生成と制御に基づいた局所反応場の設計

Microplasma jet at atmospheric pressure; Application to the rapid recrsytallization of a-Si

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1. INTRODUCTION

The rapid recrystallization of amorphous silicon a-Si has been extensively studied using laser annealing, infrared (IR)-lamp heating and rapid thermal annealing (RTA) for further enlargement of the crystalline grain size and improvement of the performance of poly-Si thin film transistors (TFTs) [1-5]. Recently, the argon microplasma jet at ambient pressure has been applied for the rapid recrystallization of a-Si. Highly crystallized poly-Si films were synthesized up to ~2-μm-thick a-Si films by adjusting the rf power P_{rf}, translating velocity of substrate stage and flow rate of Ar Fr(Ar) [6]. In this paper, we report the rapid recrystallization of a-Si and its related materials such as a-Si(P), a-Si(B), a-SiGe, and a-SiOH using rf microplasma jets of argon at ambient pressure.

2. EXPERIMENTAL

The tube electrode consisting of tungsten carbide (WC) was used as a cathode electrode with a length of 4 cm and an inner hole diameter, *d*, of 700 μm. The rf (13.56 MHz) power of 30 W was supplied to the tube electrode through the matching circuit. The electrode-substrate distance was 3 mm. In this arrangement, the WC tube was used as both the argon gas inlet and the cathode electrode. Plasma state was monitored by optical emission spectroscopy (OES) as functions of P_{rf} and Fr(Ar). A-Si, a-Si(P, B), a-SiGe, and a-SiOH films were fabricated on glass by conventional rf PE-CVD of a SiH_4-H_2 mixture at substrate temperature T_s of 250ºC by adding PH_3, B_2H_6, GeF_4, and CO_2, respectively. Plasma annealing was performed using the rf microplasma jet of Ar by translating the substrate stage at v_{sub} of 0.01-100 mm/s. Fr(Ar) was in the range from 1 to 3 *l*/min. Recrystallized Si films were characterized by X-ray diffraction (XRD), micro-Raman spectroscopy with a 5145 Å excitation line, micro-Fourier-transform infrared reflection absorption spectroscopy (FTIR-RAS), atomic force microscopy (AFM) and transmittance electron microscopy (TEM). The recrystallization process was also monitored by using the time-resolved optical reflectivity using a He-Ne laser (10 mW) at incident angle of 30º and spectroscopic ellipsometry (SE).

3. RESULTS AND DISCUSSION

Figure 1 shows Raman spectra of 5000-Å-thick recrystallized Si films annealed at different v_{sub}s and Fr(Ar)s. The Si layer was damaged and physically sputtered rapidly, resulting in a hole being formed quickly underneath the tube electrode when the v_{sub}

was below ~0.1 mm/s. Notably, the Raman peak at 518-520.5 cm^{-1} corresponding to the c-Si transverse optical (TO) phonon mode was clearly observed for v_{sub} of 0.01-250 mm/s within a 700 μm radius of the tube electrode, and the 100 μm area outside this zone was composed of a mixture of amorphous and crystalline Si. In addition, a symmetrical Raman peak at 518 cm^{-1} was observed at Fr(Ar) of 4-10 *l*/min. Thus, highly crystallized poly-Si films were formed by adjusting rf power and Fr(Ar) utilizing the rf microplasma jet at atmospheric pressure.

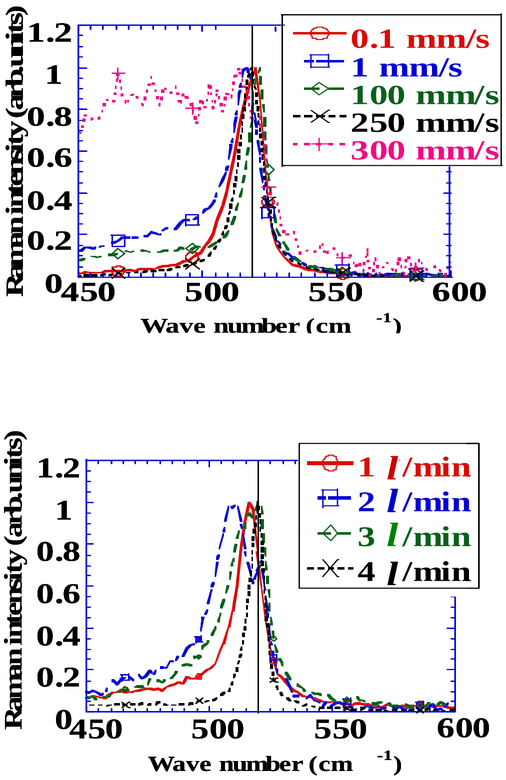

Fig. 1 Raman spectra of Si films after the plasma annealing at different v_{sub}s and Fr(Ar)s.

The plasma annealing was also performed in P and B doped a-Si films at P_{rf}; 30 W, v_{sub};1 mm/s and Fr(Ar);1 *l*/min. Electrical conductivity σ and its activation energy ΔE_σ determined from the temperature dependence of σ are also shown in Fig. 2 for corresponding n- and p-type a-Si samples before and after the Ar plasma annealing. The σ increased up to 10^3 S/cm after the plasma annealing, which were two or three orders of magnitudes higher than that of intrinsic poly-Si. As a consequent, both highly crystallized Si(P) and Si(B) films with higher electrical conductivities of 10^{1-3} S/cm were fabricated by adjusting the v_{sub} and Fr(Ar).

Figure 3 shows Raman spectra of recrystallized a-$SiGe_{0.6}$ and a-SiOH films at different Fr(Ar)s. Three peaks attributed to Ge-Ge, Si-Ge and Si-Si phonon modes were clearly observed in a-$SiGe_{0.6}$ at 300, 400 and 500 cm^{-1} after the plasma annealing. The Raman peak at 518 cm^{-1} corresponding to the c-Si was also promoted for a-SiOH. The crystallization was observed in the wide plasma conditions compared to that of a-Si, suggesting that the fine structure of the precursor also depend on the degree of the film crystallinity. The rapid recrystallization of a-Si related materials was realized by adjusting the v_{sub} and Fr(Ar).

To understand the recrystallization process of a-Si, the time evolution of the optical reflectivity were monitored using a He-Ne laser (λ=6328 Å) as a function of rf power during the Ar plasma exposure of 50 ms. The rise time and the saturated intensity of optical reflectivity corresponding to the changes of optical reflective index and temperature of a-Si depend on rf power and Fr(Ar). The optical reflectivity increased with time during 50 ms at P_{rf} below 20 W. It rapidly increased during 10-15 ms and tended to saturate at P_{rf} over 20 W. Low Fr(Ar) of 1-2 *l*/min also shorten the rise time and shows higher intensity of the optical reflectivity because the plasma temperature was higher. In addition, the real time SE study of the recrystallization of a-Si by the plasma annealing revealed that the fine structures at 3.4 and 4.3 eV attributed to the E_1 and E_2 optical band transitions, respectively, of c-Si band structure were observed after the 15 ms when the rf plasma was turned on, suggesting that the solid-phase crystallization (SPC) occurred. These results suggest that the SPC proceeds quickly after 10-15 ms during the plasma exposure.

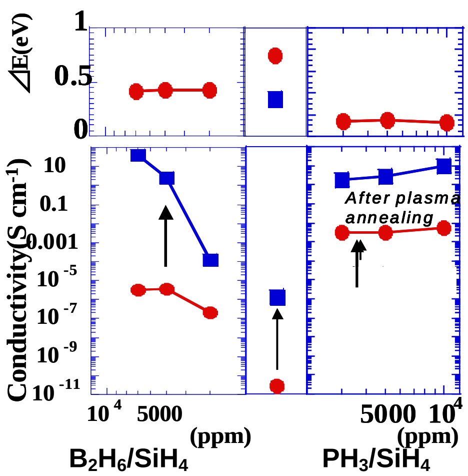

Fig. 2 Electrical conductivities and its activation energy of a-Si(P,B) films before and after plasma annealing.

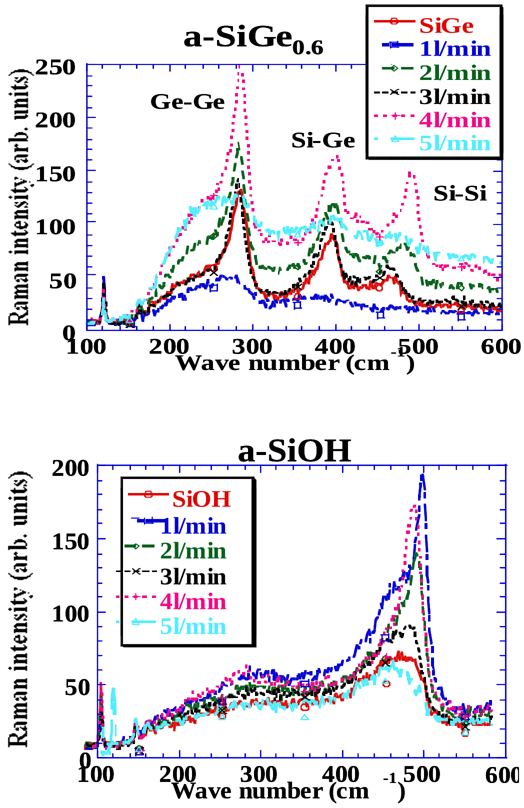

Fig. 3 Raman spectra of SiGe and SiOH films after plasma annealing at different Fr(Ar)s.

4. DISCUSSION

In addition to the rapid recrystallization of a-Si, the impurity activations of P and B were also promoted as shown in Fig. 2, although the Raman crystallinity of a-Si(B) films was deteriorated rather than the intrinsic a-Si and a-Si(P).The rapid recrystallization of a-Si and its related alloys, a-SiGe, and a-SiOH were performed utilizing the rf plasma jet of argon by adjusting the P_{rf}, v_{sub}, and Fr(Ar) (Figs. 1and 3). These suggest that the fine structure of a-Si network used for the precursor also influences the degrees of the film crystallinity. In fact, the a-SiOH and a-SiGe films were highly recrystallized in the wide plasma annealing conditions compared with those of a-Si.

To understand the recrystallization mechanism of a-Si using the Ar microplasma jet, the time evolution of the optical reflectivity of a He-Ne laser and the SE spectra were monitored as functions of P_{rf} and Fr(Ar). The real time SE measurement revealed that the recrystallization of a-Si and its alloy materials proceeded quickly after 10-15 ms plasma exposure, which showed much longer time constants compared to that of laser annealing of 20-50 ns. On the other hand, the rise time of the reflective intensity was in the range of 10-50 ms. On the other hand, the degree of the film crystallinity depends on the reflective intensity of a He-Ne laser, suggesting that it is mostly determined by the electron temperature T_e. In addition, the OES emission intensity of ArI 750.4 nm corresponding to the electron density n_e showed a maximum at Fr(Ar) of 4 *l*/min and subsequently it tended to decrease, when a *d* was 700 μm. The gas excitation temperature T_{ex} of the rf plasma jet of Ar was 3000-7000 K and at increasing Fr(Ar) tended to decrease T_{ex}~T_e. Thus, there exists an appropriate flow velocity of Ar for promoting the recrystallization of a-Si. The Raman intensity ratio $I_c/(I_{nc}+I_c)$ was also markedly enhanced at Fr(Ar) of 4 *l*/min at P_{rf} of 30W. From tehse results, high n_e and high T_e plasma is effective for the rapid recrystallization of a-Si, although the degree of the film crystallinity also depend on the fine structure of the film precursors.

The three-dimensional numerical simulation of heat transfer and fluid flow of argon suggested that the gas temperature T_g reached 2000-2500 K during 0.15 ms at the substrate surface, 3 mm away from the tube electrode, when the Ar flux with T_g of 5000 K was supplied at v_d of 1 *l*/min. However, the optical reflectivity changed with a long time constant with 10-50 ms. Therefore, the degree of the film crystallinity is determined by not only plasma condition but also the thermal conductivity, heat capacity and atomic density of a-Si as well as the degree of the disorder of a-Si network of the precursors.

5. CONCLUSION

An rf microplasma jet at atmospheric pressure using Ar can rapidly and effectively crystallize a-Si. In addition to the rapid recrystallizaition of a-Si and its related alloy materials, a-SiGe and a-SiOH to poly-Si and SiGe, the impurity activation of P and B atoms were also promoted by the rf plasma. The high electron-density and high electron-temperature plasma source is available for the rapid recrystallization of a-Si and its related materials.