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High-Rate Growth of Highly-Crystallized Si Films from VHF Inductively-Coupled Plasma CVD

Nihan Kosku and Seiichi Miyazaki
Graduate School of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8530, Japan
Fax: 81-824-227-038, e-mail: nihan@hiroshima-u.ac.jp

H_2-diluted SiH_4 inductively-coupled plasma (ICP) generated by VHF (60MHz) power, which enables us to form highly-crystallized Si films at a deposition rate as high as a few nm/s, has been studied in comparison with H_2-diluted SiH_4 ICP generated by RF (13.56MHz) power. Using optical emission spectroscopy (OES), Si, SiH, H_α, H_β and H_2 were monitored while varying different deposition parameters such as the total flow rate, the power density and the SiH_4 concentration (R= $[SiH_4]/([H_2]+[SiH_4])$). An intense light emission from VHF-ICP confirms an efficient gas excitation and dissociation compared to the case of RF-ICP. Even when the SiH_4 concentration is increased up to 20%, atomic hydrogen intensity in the VHF ICP remains nearly constant while it decreases linearly in RF ICP, which indicates sufficient atomic hydrogen to promote the surface migration of the precursors in VHF-ICP. It is found that the OES intensity and the intensity ratio of H_β to H_α are correlated with the deposition rate and the crystallinity, respectively. By increasing the power density up to 4.3W/cm^2, the growth rate of crystallized Si films is enhanced to ~10nm/s.

Key words: VHF Inductively coupled plasma; Microcrystalline silicon; High rate deposition; Optical emission spectroscopy

1. INTRODUCTION

The growth of crystalline silicon thin films on glass or plastic substrates has taken a great interest for large-scaled electronic device applications such as thin-film solar cells as well as thin film transistors (TFTs) because of the higher mobility and stability of the crystallized films in comparison with those of amorphous silicon films (a-Si:H) [1, 2]. In addition to this, because the optical absorption of microcrystalline silicon films is enhanced by optical confinement due to internal multiple scattering especially in the near-infrared region, microcrystalline silicon-based solar cells show considerable high efficiencies without light-induced degradation [3, 4]. Since the high deposition rate of crystalline films at low substrate temperatures is one of the major concerns to improve the quality and the performance of these devices with a low cost, so far a number of approaches have been reported. To obtain a relatively high flux of hydrogen radicals at a high growth rate, different high-density plasma generation techniques such as very high frequency (VHF) [5] and ultra-high frequency (UHF) plasmas [6], electron cyclotron resonance (ECR) plasma [7] and microwave plasma [8] have been studied. Despite many efforts, uniform growth of highly crystallized without any powder formation and ion damages is still a matter of research. In our previous work, we demonstrated the feasibility of inductively coupled plasma (ICP) generated by an RF power for a high-rate (>1nm/s) deposition of crystalline Si and Ge films [9, 10].

In this study, to further increase the deposition rate without external magnetic field with keeping the deposition uniformity and avoiding powder formation, we extended our research work to the diagnostics of VHF inductively-coupled plasma by using optical emission spectroscopy (OES) and compared the results to those from RF-ICP.

2. EXPERIMENTAL

The inductively-coupled plasma of H_2-diluted SiH_4 was generated by an external single-turn antenna with a diameter of ~12cm, which was placed on a 1cm-thick quartz plate window and connected with a power supply. The distance between the antenna and the substrate temperature were maintained at 45mm and 250°C, respectively. Si:H films were deposited on quartz, Cr-evaporated Si(100) and HF-last Si(100) substrates, placed on the stainless steel susceptor (12.5cm in diameter). OES was carried out in the wavelength range of 200-700nm, to assess the gas dissociation in ICP and find out the conditions for higher growth rate with keeping a high crystallinity. The SiH_4 concentration (R= $[SiH_4]/([H_2]+[SiH_4])$) was varied in the ranges of 12-22% at a constant gas flow rate of 150sccm and gas pressure of 90mTorr for the films deposited from VHF-ICP. For the case of RF-ICP, the gas flow rate and the gas pressure were reduced to 100sccm and 60mTorr, respectively, because the crystalline film growth is hardly observed at exactly the same flow rate and pressure as VHF-ICP above-mentioned. In addition, at a SiH_4 concentration fixed at 12%, the total gas flow rate was varied from 100 to 175sccm in VHF-ICP. The VHF and RF power density was changed in the range of 2.6-4.3W/cm^2 and 2.0-3.2W/cm^2, respectively. For direct characterization of the network structure of the Si films so prepared, the Raman scattering spectra were measured under a right-angle scattering geometry, in which a p-polarized 441.6 nm light from a He-Cd laser was incident to the sample surface in Ar ambience at a glancing angle of about 10°. Hydrogen content in the films was measured by Fourier transform infrared (FT-IR) spectroscopy.

3. RESULTS & DISCUSSION

In VHF-ICP, Raman spectra of the films confirm the crystalline film growth in the SiH_4 concentration range of R=12-20% and amorphous film growth at R=22% as shown in the inset of Fig. 1. At R=12%, the crystalline network, in which the TO phonon intensity ratio of the crystalline peaks at ~518cm^{-1} to the disordered component at ~480cm^{-1} is as high as 5, is formed with a growth rate of ~3.3nm/s as represented in Fig. 1. When the SiH_4 concentration becomes 15%, the growth rate is increased to ~6nm/s with little degradation in crystallinity. With a further increase of the SiH_4 concentration to 20%, the crystallinity degrades slightly while the growth rate increases to almost ~7.2nm/s which is 7 times as large as the value obtained by RF-ICP [9]. The formation of amorphous network at R=22% shown by the broad Raman scattering spectrum, can be explained in terms that the flux of hydrogen radicals to film precursors incident to the growing film surface is insufficient to promote the surface migration of the precursors.

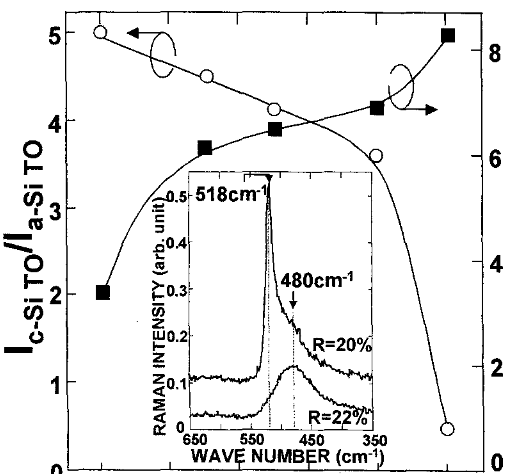

Fig. 1 Intensity ratio of the TO phonon mode peaked at ~518cm^{-1} to that at ~480cm^{-1} and the deposition rate as a function of SiH_4 concentration. The power was fixed at 3.1W/cm^2. In the inset Raman scattering spectra for ~2μm-thick Si:H films grown with 20 and 22% of SiH_4 concentrations.

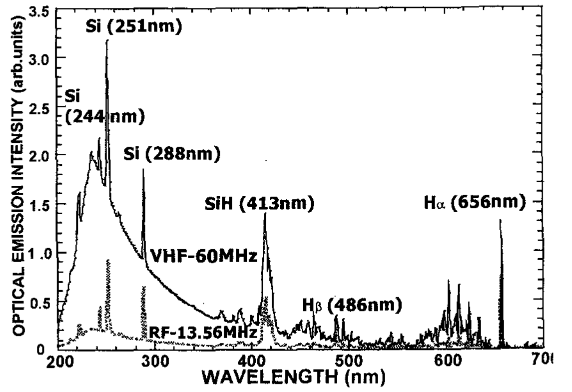

Fig. 2 Optical Emission Spectra for RF and VHF ICPs at a total gas flow rate of 150sccm and a SiH_4 concentration of 20%. The spectra of RF-ICP is enlarged by a factor of 10.

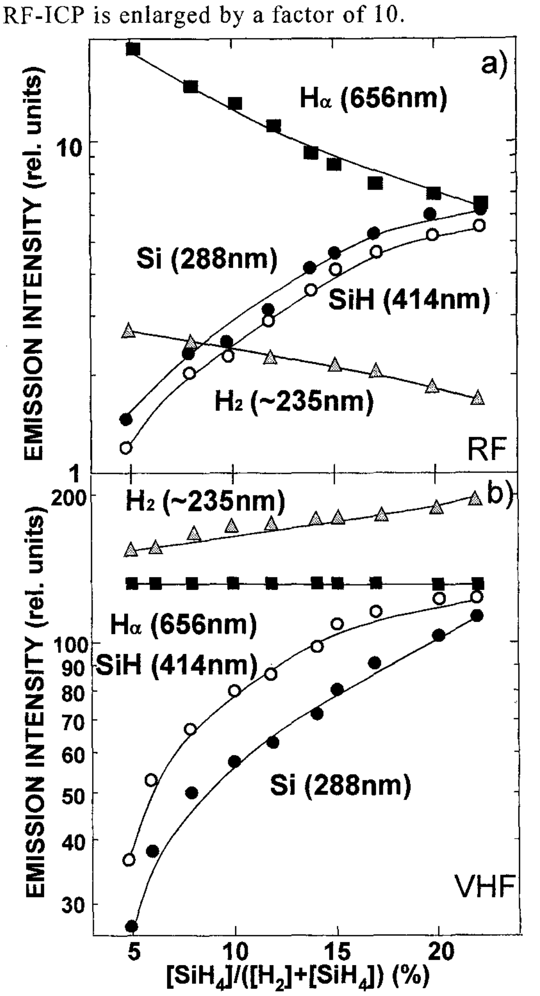

Fig. 3 Optical emission intensities of Si (288nm), SiH (414nm), H_α (656nm) and H_2 (~235nm) as a function of SiH_4 concentration for RF (a) and VHF ICP's (b) for the films seen in Fig. 1.

The significant improvement in the growth rate of crystalline films in the VHF-plasma can be interpreted by a large increase in the excitation and dissociation rate as confirmed from optical emission spectra of VHF-ICP at a SiH_4 concentration of 20% in comparison to those of RF-ICP as shown in Fig. 2. Fig. 3 shows the

SiH_4 concentration dependence of the emission due to Si, SiH, H_α and H_2 in RF- and VHF-ICP at the same power density of ~3.1W/cm^2. The H_β emission intensity is not included in the figure because the dependence on the SiH_4 concentration is similar to the H_α emission intensity. The extremely intense emissions from VHF-ICP are observed particularly as the SiH_4 concentration exceeds 10%. Notice that, with increasing SiH_4 concentration, the H_α emission intensity almost remains unchanged in VHF-ICP, but in contrast it is markedly decreased in the RF-ICP. In addition, the SiH emission intensity is higher than the Si emission intensity in VHF-ICP and the opposite result for RF-ICP, which may reflect the difference in the hydrogen content between films from VHF- and RF-ICPs as will be discussed later. Another remarkable difference between VHF- and RF-ICPs is seen in the SiH_4 concentration dependence of the emission from hydrogen molecules, which indicates efficient generation of H_2 due to the Si network formation in VHF-ICP compared with the RF-ICP case.

To gain a better understanding of the crystalline film formation, we examined the influence of total gas flow rate on the deposition rate and the crystallinity of the films and discussed the correlation between the OES intensity ratio of H_α to SiH in VHF-ICP as shown in Fig. 4. With increasing the flow rate, the crystallinity improves accompanied with an increase in the growth rate until it becomes its maximum (~6) at 120sccm and then degrades remarkably. The less crystallinity obtained in the lower flow rate side suggests that, in both cases, etching reactions due to hydrogen radicals and ions are more significant at a lower flow rate which can be explained by the high dissociation rate as confirmed from the high ratio of H_α to the

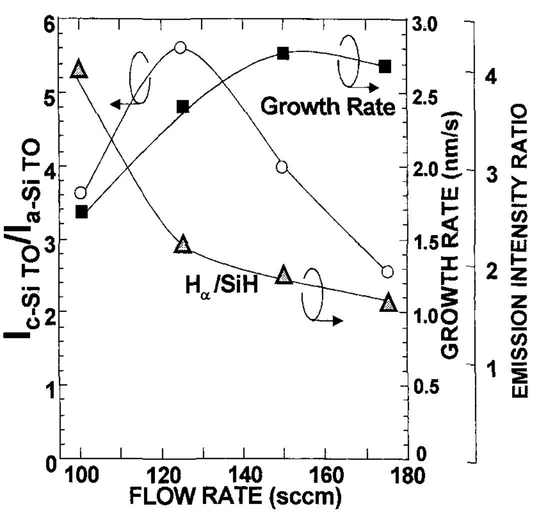

Fig. 4 Intensity ratio of the TO phonon mode peaked at ~518cm^{-1} to that at ~480cm^{-1} the deposition rate and emission intensity ratio of H_α to SiH as a function of the total gas flow. The ICP of 12% SiH_4 is generated at 2.6W/cm^2.

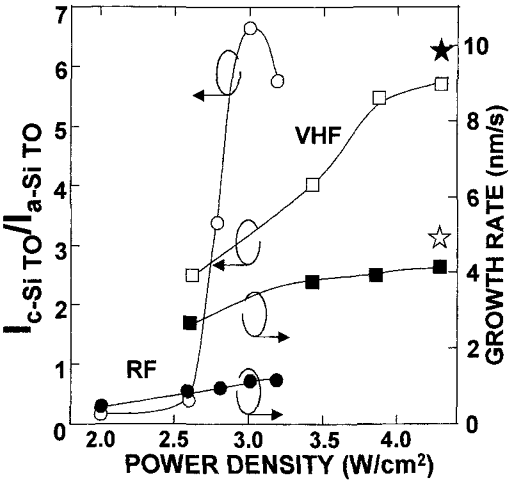

Fig. 5. Intensity ratio of the TO phonon mode peaked at ~518cm^{-1} to that at ~480cm^{-1} and the deposition rate as a function of the power density. The ICP of 12% SiH_4 is generated from total gas flow of 175sccm. The open and closed stars correspond to the crystallinity and the deposition rate, respectively at a SiH_4 concentration of 20%.

total flow rate (Fig. 4). When the flow rate becomes larger than 120sccm, the growth rate tends to be saturated and decreases slightly over 150sccm. Therefore the deterioration of the crystallinity can be interpreted in terms that the flux of atomic hydrogen incident to the growing film surface with respect to the flux of the film precursors is insufficient to promote the structural relaxation for the microcrystalline formation as suggested from the decrease in the ratio of H_α to SiH. The diffusion loss of generated precursors, mainly the H radicals may partly contribute to a reduction in the deposition rate. In addition, as the flow rate increases, a decrease in electron temperature is confirmed from the decrease in the ratio of H_β to H_α.

At high flow rates to improve the crystallinity at a high rate deposition with promotion of the gas dissociation, the input power was increased from 2.6 to 4.3W/cm^2 in VHF-ICP and from 2.0 to 3.2W/cm^2 in RF-ICP as shown in Fig. 5. As expected, the crystallinity almost completely recovers even at a growth rate as high as 4nm/s in the VHF-ICP. At 4.3W/cm^2 when the SiH_4 concentration is increased from 12% to 20% the growth rate reached ~10nm/s which was 10 times as large as the value obtained by RF-ICP [9] although the crystallinity was degraded to ~3. Notice that, for the RF-ICP, the deposition rate does not exceed 1.2nm/s even if the power density was increased and in the power density region higher than 3.0W/cm^2, a decrease in the growth rate and the degradation of the crystallinity were observable, implying that ion damages become significant because of higher electron temperature than the case of VHF-ICP.

Hydrogen incorporation into the films was characterized by FT-IR measurements for films

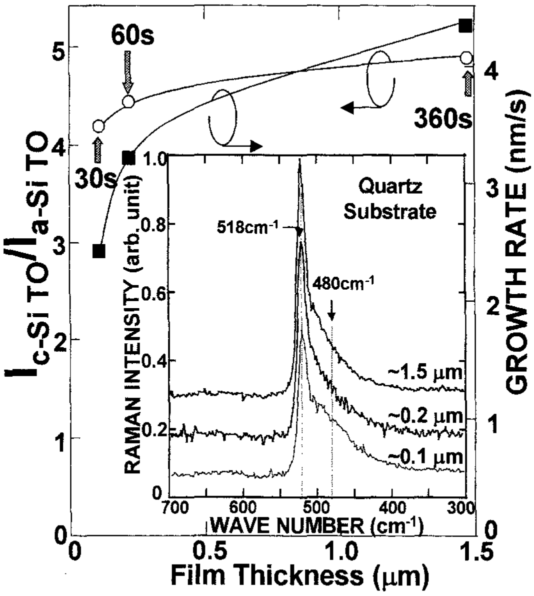

Figure 6. Intensity ratio of the TO phonon mode peaked at ~518cm^{-1} to that at ~480cm^{-1} and the deposition rate as a function of the film thickness. Raman scattering spectra for Si:H films grown at 12% SiH_4 with different film thicknesses are also shown in the inset.

thicker than 2μm. The hydrogen concentration in the films deposited from VHF-ICP does not exceed 4 at.% even for amorphous films and it decreases down to 1~2 at.% for highly-crystallized films. On the other hand, the highly-crystallized films grown from RF-ICP have a hydrogen content as high as ~3 at.% in average. Since hydrogen atoms are incorporated mainly into the disordered incubation layer formed in the early stages of the film growth and partly into the grain boundaries, we can suggest that incubation layer prior to the crystalline nucleation is thinner for the films deposited from VHF-ICP. In fact, a distinct evolution of the crystalline phase with progressive film growth on quartz, is observable even after 25s deposition which corresponds to 100nm in thickness being much thinner than the case of RF-ICP (>200nm). Also, for both the cases of VHF- and RF-ICPs, no absorption due to oxygen incorporation, if any in the wavelength range of 1050-950cm^{-1}, was measured within a detection limit of the IR measurements (below 0.1at%). From the XRD measurements the crystallite grain sizes of the films deposited from RF- and VHF-ICPs are determined to be ~10nm and ~20nm, respectively. Highly-crystallized Si:H films deposited from VHF-ICP show an optical band gap of ~1.5eV with a conductivity activation energy of ~0.5eV. Since the activation energy is larger than that obtained for crystallized films from RF-ICP (~0.3eV) [9], it is likely that the crystalline network with less defects and/or the grain boundaries well-passivated with H atoms are formed by VHF-ICP. Correspondingly, for the crystallized films deposited from VHF-ICP, a photoconductivity in the range of 0.1~0.2mS/cm and a photosensitivity of 50~130 under AM1 (100mW/cm^2) illumination were obtained, indicating better film quality than crystallized films from RF-ICP [4] which possess a photoconductivity of 0.01~0.1mS/cm with a photosensitivity of ~3-10.

4. CONCLUSIONS

We have confirmed that VHF-ICP has a high potential to achieve high deposition rates of highly crystallized films without any powder formation. By using a VHF-ICP at a SiH_4 concentration of 20%, crystallized films, where Raman scattering intensity ratio of the crystalline TO-phonon peak to the disordered component is higher than ~3, are formed at a deposition rate as high as ~10nm/s which is ~10 times larger than the rate obtained by RF-ICP. From the OES results, we elucidated an efficient gas excitation and dissociation rate in VHF-ICP compared to RF-ICP and a high relative flux of H radicals which do not decrease even at high SiH_4 concentrations. We have also demonstrated that the total gas flow rate and the power density also play a crucial role for the improvement in the crystallinity and the growth rate of the films. The crystallinity and the growth rate, in higher flow rate conditions in VHF-ICP, is markedly improved with an increase in the input power.

5. ACKNOWLEDGEMENTS

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