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

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1. Introduction

The low temperature growth of crystallized silicon-based films is attracting much attention because of its technological importance for thin-film solar cells with stable conversion efficiencies [1] as well as thin film transistors (TFTs) with a higher performance than amorphous Si TFTs [2]. Especially, high-rate growth of highly-crystallized active layer is a crucial factor for industrial mass productions. In that regard, the use of high-density plasma and its practical advantages have been demonstrated so far [3]. However, uniform and high-rate deposition of highly-crystallized Si films without any powder formation is still a matter of research. Previously, we reported 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 [4, 5].

In this study, we extended our work to the crystalline Si film growth from VHF ICP to further increase the deposition rate without external magnetic field.

2. Experimental

The VHF plasma of H_2-diluted SiH_4 was generated by an external single-turn antenna with a diameter of ~12cm, which was placed on the quartz window and connected with a 60MHz power supply. The distance between the antenna and substrates such as quartz, corning and HF-last Si(100) and the substrate temperature were maintained at 45mm and 250ºC, respectively. 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. At R=12%, the total gas flow rate was varied from 100 to 175sccm. The VHF power density was changed in the range of 2.6-4.3W/cm^2. 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 an He-Cd laser was incident to the sample surface in Ar ambient at a glancing angle of about 10º.

3. Results and Discussion

Raman spectra of the films confirm the growth of highly crystallized films in the SiH_4 concentration range below 20% as shown in Fig. 1. In the case of R=12%, the crystallinity, which was determined by the TO-phonon intensity ratio of the crystalline phase to the disordered one, as high as 5 and a growth rate of ~3.3nm/s were obtained (Fig. 2). With increasing SiH_4 concentration to 20% in VHF-plasma, the growth rate reached ~7nm/s which was 7 times as large as the value obtained by RF-ICP although the crystallinity was degraded slightly to 3.7. Further increase in the SiH_4 concentration causes amorphous network

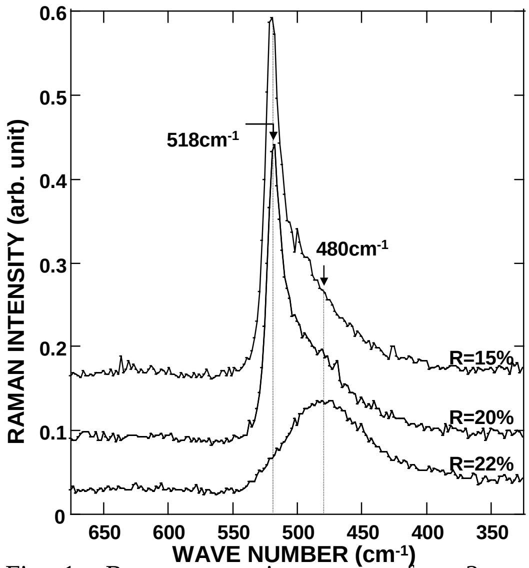

Fig. 1 Raman scattering spectra for ~2µm-thick Si:H films grown with different silane concentrations. The VHF power was fixed at 3.1W/cm^2.

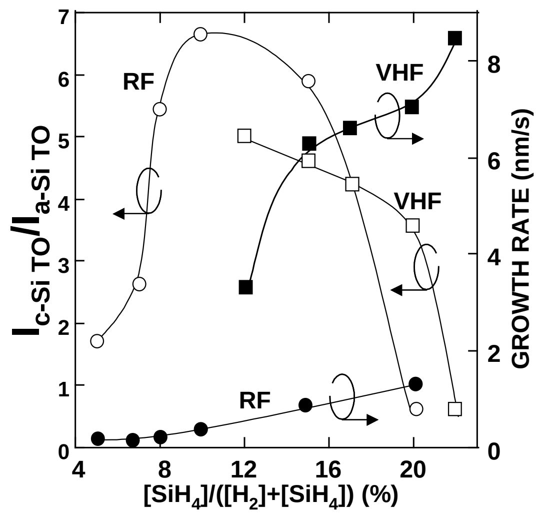

Fig. 2 Intensity ratio of the TO phonon mode peaked at ~518cm^{-1} to that at ~480cm^{-1} and the deposition rate as a function of SiH_4 concentration. The open and closed squares represent the results obtained for the VHF plasma. The results obtained for the RF plasma, where the flow rate and the gas pressure was maintained at 100sccm and 60mTorr, respectively, are also shown with the open and closed circles.

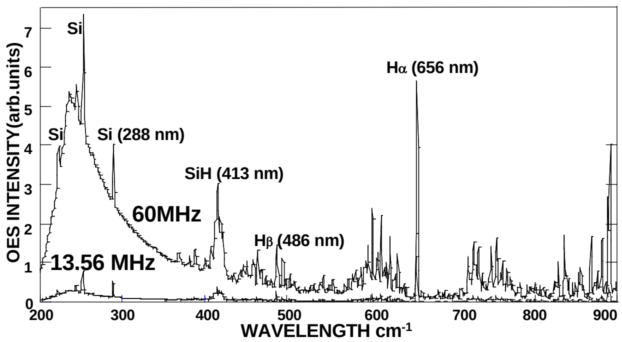

Fig. 3 Optical Emission Spectra for RF and VHF ICPs at a total gas flow rate of 150sccm and a SiH_4 concentration of 12% with a power density of $2.6W/cm^2$.

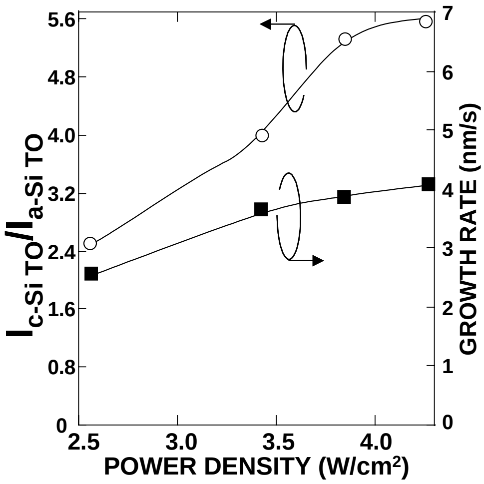

Fig. 5 Intensity ratio of the TO to TA phonon and the deposition rate as a function of the VHF power density. The ICP of 12% SiH_4 is generated from 175sccm of total flow rate.

formation presumably because the relative flux of hydrogen radicals to film precursors incident to the growing film surface becomes insufficient to promote the surface migration of the precursors. The significantly increased growth rate in comparison with RF-ICP cases can be explained by an efficient gas excitation and dissociation in the VHF plasma as confirmed from optical emission spectra where the emission intensities due to atomic Si, SiH, atomic H and molecular H_2 are observable as shown in Fig. 3.

To gain a better understanding of the cystalline film formation, we examined the influence of total gas flow rate on the deposition rate and the crystallinity of the films in both the RF- and VHF-ICPs as indicated in Fig. 4. In the VHF-ICP, with increasing flow rate, the crystallinity improves accompanied with an increase in the growth rate until becomes its maximum (5.6) and then degrades quickly. A similar flow rate dependence of the growth rate in the relatively low flow rate region is observable for the RF-ICP case, reflecting less dissociation rate in the RF-ICP compared with the VHF-ICP. The flow rate

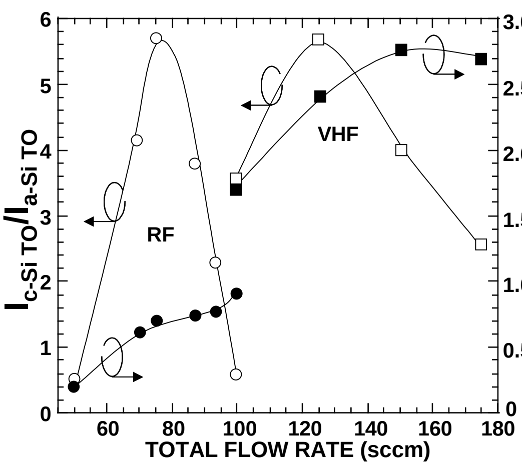

Fig. 4 The intensity ratio of the TO to TA phonon mode and the deposition rate as a function of the total gas flow rate for both RF (open and closed circles) and VHF-ICP (open and closed squares). The ICP of 12% SiH_4 is generated with $2.6W/cm^2$.

dependence in a lower flow rate region suggests that in each case etching reactions due to hydrogen radicals and ions are more significant at a lower flow rate. Since, in the flow rate region higher than 120sccm for VHF-ICP, the growth rate tends to be saturated and decreases slightly over 150sccm, the deterioration of the crystallinity can be interpreted in terms of a decrease in the gas dissociation rate, namely a decrease in the generation rate of atomic hydrogen, due to a decrease in electron temperature as confirmed from optical emission measurements. In fact, when the VHF power density is increased up to $4.3W/cm^2$, the crystallinity almost completely recovers at a growth rate as high as 4nm/s.

For even highly-crystallized Si:H films, an optical band gap of ~1.5eV and a photoconductivity in the range of 1~0.1mS/cm with a photosensitivity of 30~200 were obtained under AM1 ($100mW/cm^2$) illumination.

4. Conclusions

We have demonstrated that the use of VHF-ICP is a promising way to achieve high deposition rates of highly crystallized films without any powder formation. The control of the SiH_4 concentration is of great importance for higher crystallinity at higher deposition rate. The total gas flow rate and the power density also play a crucial role for the improvent in the crystallinity and the growth rate of the films.

References

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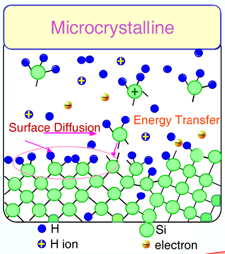
ABSTRACT

We have investigated the high-rate microcrystalline silicon (μc-Si:H) formation from inductively-coupled plasma (ICP) of monosilane (SiH_4) diluted with hydrogen at 250°C and compared the results obtained from RF (13.56MHz) and VHF (60MHz) ICP. By using a VHF-ICP at a SiH_4 concentration of 20%, highly-crystallized films, where Raman scattering intensity ratio of the crystalline TO-phonon peak to the disordered component is higher than ~4, are formed at a deposition rate as high as ~7.2nm/s which is ~7 times larger than the rate obtained by RF-ICP in the same input power. Based on the optical emission measurements, the result is attributable to a high generation rate of hydrogen radicals resulting from the efficient SiH_4 and H_2 decomposition in a VHF plasma. From the gas flow rate dependence of the crystallinity we have found that VHF-ICP enables us to prepare the crystalline films at higher gas flow rates than RF-ICP, which results in a remarkable increase in the growth rate. We have also demonstrated that the crystallinity, in higher flow rate conditions especially in VHF-ICP, is markedly improved with an increase in the input power.

Background

Microcrystalline Silicon Thin Films: ***Large Area TFT & Solar Cells***



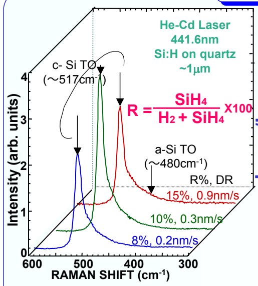
ADVANTAGES in Comparison to Amorphous Si:

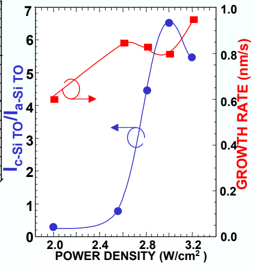
- **Long Term Stability**
- **Enhanced Carrier Mobility**
- **Superior Optical Confinement**

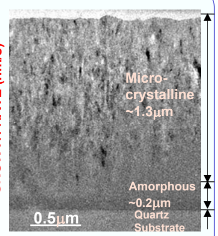
Requirements:

- **High-Rate Deposition>2nm/s**
- **Low Temperature Process<250°C**
- **Uniform, Large-Area Film Deposition**
- **No Powder Formation**

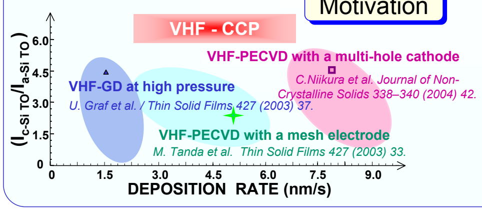
Characteristics of RF-ICP







Motivation



RF - ICP

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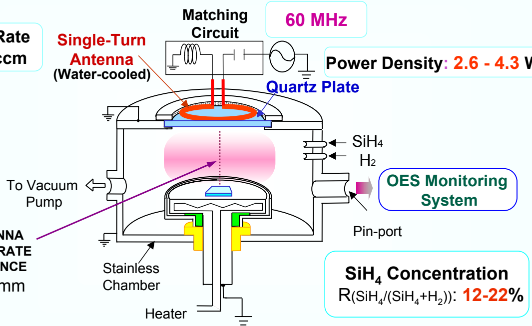
VHF - ICP

Experimental

ICP CVD System

Total Flow Rate
100 - 175sccm



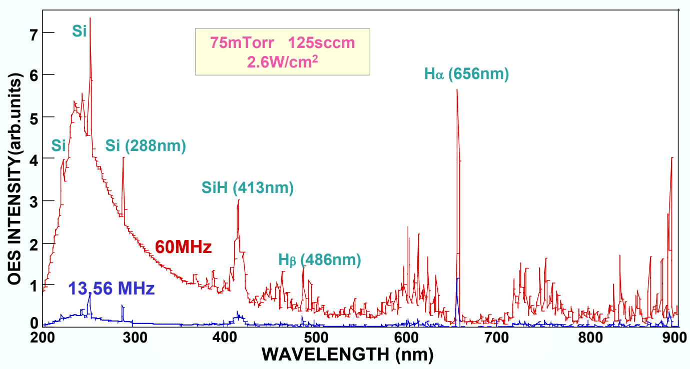
Power Density: 2.6 - 4.3 W/cm²

ANTENNA SUBSTRATE DISTANCE
z = 45mm

SiH_4 Concentration
R(SiH_4/(SiH_4+H_2)): **12-22%**

Substrate Temperature: **250°C**

Optical Emission Spectra, RF-VHF

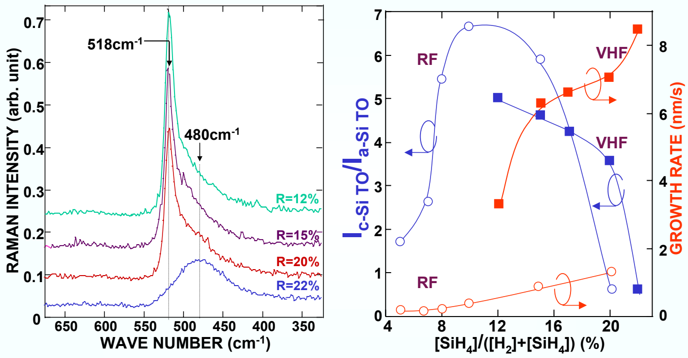


Higher generation rate of radicals in VHF-ICP than RF-ICP

Crystallinity & Growth Rate at Different SiH_4 Concentrations (R)

VHF 90mTorr, 150sccm 3W/cm²

RF 60mTorr, 100sccm, 3W/cm²

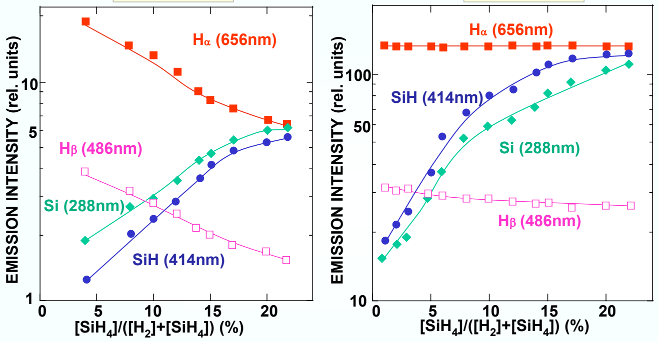


For VHF-ICP the crystalline film is grown at ~7.2nm/s which is 7 times as large as the value obtained by RF-ICP

Optical Emission Intensities vs. SiH_4 Concentration (R)

RF - ICP

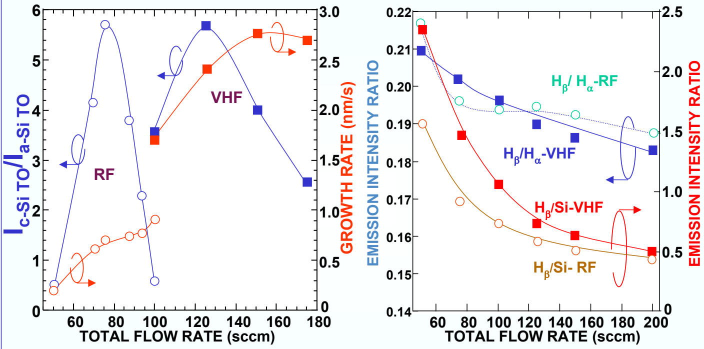
VHF - ICP



With increasing SiH_4 concentration, in the VHF-ICP, the emission intensity of H_α & H_β almost remain unchanged but in the RF-ICP the flux intensities are markedly decreased.

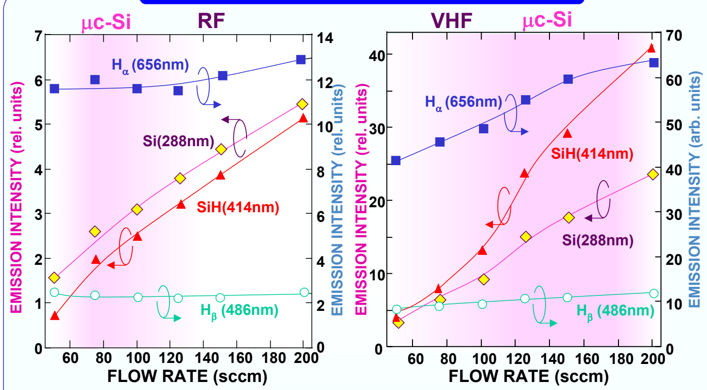
Total Flow Rate Dependence

VHF-ICP [SiH4]=12% 2.6 W/cm²



At higher flow rates, deterioration of the crystallinity is interpreted by a decrease of atomic hydrogen compared to film precursors, due to a decrease in electron temperature ~(H_β/ H_α).

Optical Emission Intensities vs. Total Flow Rate

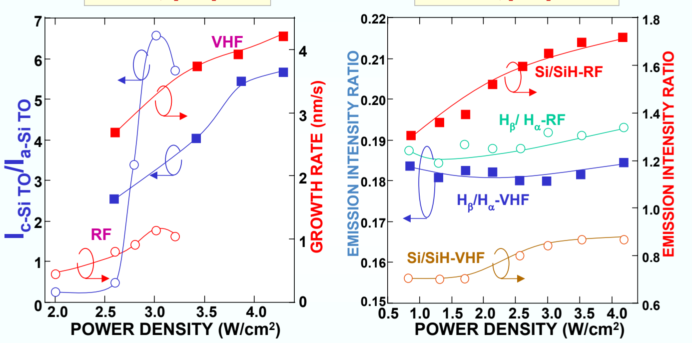


Lower electron temperature in VHF-ICP is accompanied with a higher SiH emission intensity than the Si emission, different from the case of the RF-ICP where Si is considered to cause dangling bonds.

Power Density Dependence

VHF 105mTorr, 175sccm, [SiH4] = 12%

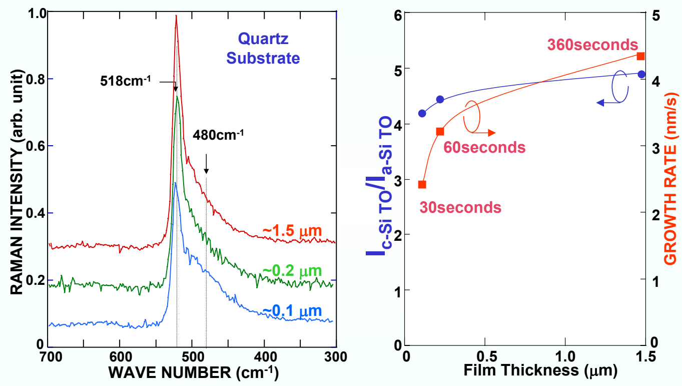
RF 60mTorr, 100sccm, [SiH4] = 12%



By the increase in input power, the crystallinity recovers at a growth rate as high as 4nm/s in the VHF-ICP even at high flow rates.

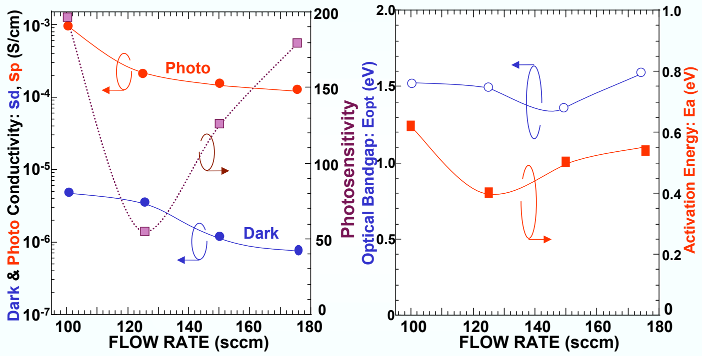
Structural Change with Progressive Film Growth

90 mTorr 150 sccm 3.8 W/cm²

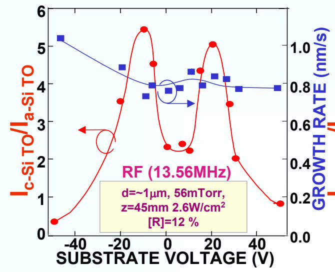


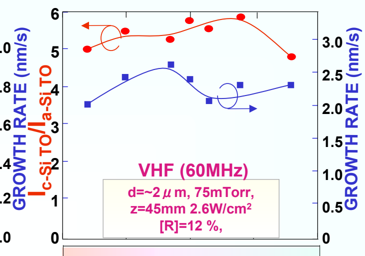
The incubation layer thickness is much lower than 100nm.

Electrical and Optical Properties vs. Flow Rate - VHF



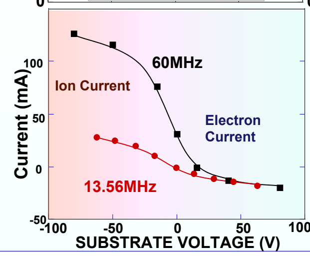
Influence of DC Bias on Crystallinity & Growth Rate- RF & VHF ICP





RF-ICP: Crystallization by the incidence of electrons or ions

VHF-ICP: Less DC-Bias Dependence



Conclusions

- Efficient gas excitation and dissociation rate in VHF-ICP compared to RF-ICP
- μc-Si:H film growth from VHF-ICP at a growth rate as high as ~7.2nm/s with a crystallinity of ~4 at SiH_4 concentration of 20%
- At flow rates >150sccm, an increased VHF power density of 4.3W/cm^2 enhances crystallinity up to 5.6 with a growth rate of 4nm/s
- Optical band gap of ~1.5eV and a photoconductivity in the range of 0.1~1mS/cm with a photosensitivity of 50~130 under AM1 (100mW/cm^2)

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