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FORMATION KINETICS AND CONTROL OF MICROCRYSTALLITE IN μc-Si:H FROM GLOW DISCHARGE PLASMA

A. MATSUDA

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The formation kinetics of μc-Si:H has been investigated through the film depositions and plasma diagnoses in widely-scanned glow discharge plasma conditions; RF power density, SiH_4/H_2 ratio and substrate temperature. The roles of H and SiH_x adsorbed on the surface as well as impinging ions have been discussed in relation to volume fraction and crystallite size of μc films, and continuous control of crystallite size has been demonstrated using a triode system. Hall mobility of the deposited μc-Si:H films has also been presented as a function of the volume fraction of μc.

1. INTRODUCTION

Amorphous-microcrystalline mixed-phase hydrogenated silicon (μc-Si:H) has attracted increasing attention as a new-phase material for thin film device applications such as solar cells and thin film transistors[1-3]. Since the initial work of Veprek and his coworkers[4] was reported, several groups have published the preparation of μc-Si:H by chemical transport[5], glow-discharge decomposition of SiH_4 diluted in H_2 or inert gas[6-8] and reactive sputtering techniques[9]. However, a detailed growth kinetics of the material has not yet been well understood. This paper, focusing on μc-Si:H via glow-discharge plasma, presents the key plasma conditions for the formation of μc-Si:H, the effect of H and ions both on the deposition mechanism and the nature of microcrystallites (μc) in the film through the deposition experiments performed under widely-scanned plasmas with the aid of the plasma diagnoses, OES and mass spectrometry. On the basis of the results, a wider-range control of crystallite size in μc-Si:H is demonstrated using the triode glow-discharge system.

2. EXPERIMENTAL

Deposition of μc-Si:H was carried out using conventional capacitively-coupled glow discharge system. Mixed SiH_4/H_2 starting gas was introduced into the evacuated (1×10^{-7} Torr) chamber at the constant flow rate (1SCCM) of SiH_4, and the total gas pressure was kept at 50mTorr. By scanning a wide range of plasma parameters, from 0.01 to 2W/cm^2 in RF power density and 1/2 to 1/49 in SiH_4/H_2 flow-rate ratio, the formation kinetics of μc-Si:H were systematically investigated. Unless otherwise specified, each sample, around 1μm in thickness, was deposited on the glass substrate as well as crystal Si wafer set on the anode electrode heated at T_s in the range of 150 to 500C.

Optical emission spectroscopy (OES) as well as mass ion spectrometry (MS) was employed as the plasma diagnostic techniques during the film deposition; the details of these measurements have been reported earlier[10]. The films were characterized through measurements of dark conductivity (σ_d), Hall mobility (μ_H), deposition rate and X-ray diffraction; crystallite size (δ), relative lattice expansion ($\Delta a/a_0$) and volume fraction (X_c) of μc in each film were determined from FWHM, 2θ-angle shift and integrated intensity of the measured X-ray diffraction line.

3. RESULTS AND DISCUSSION

3.1. T_s dependence of the film structure

Figure 1 shows the volume fraction (X_c) and the size (δ) of microcrystallites, the bonded H content (C_H) and the deposition rate of the films deposited at different substrate temperatures (T_s). Three different plasma conditions given in the figure were selected from the periphery of the μc-forming region on the map of Fig.2, whereby one can expect a drastic change in the film structure depending on T_s. As shown in the figure, X_c reveals a strong dependence on T_s, taking a maximum value at around 400C and tending to zero at a lower as well as higher T_s range. It should be noted that the growth rate is almost independent of T_s while C_H decreases monotonously with an increase of T_s, coming down to zero at 500C.

In general, admolecule (adsorbate) has a thermally-activated surface-diffusion coefficient (D_s) described as

$$D_s \propto a^2 \exp(-E_s/kT),$$

where a is the jump distance between the adsorption sites, and E_s the activation energy for a surface-diffusion jump[11]. Therefore, a crystalline-to-amorphous transition at a lower T_s range might originate from a decreasing D_s of SiH_x adsorbates because they cannot diffuse into stable sites for μc nuclei formation. Desorption of adsorbates is also in a thermally-activated process but, in a whole T_s range scanned in the present work, SiH_x adsorbates presumably do not desorb from the growing surface at least within a deposition time of a monomolecular layer, judging from a constant deposition rate over a whole T_s range shown in the bottom figure. This speculation is compatible with the statement by Veprek et. al.[5] that the plasma etching could be negligible for the surface reaction in Si:H deposition from SiH_4 glow discharge[5]. In contrast to SiH_x, H-elimination reaction takes place depending strongly on T_s, as is clear from the data of C_H. It is quite possible that the amount of H covering the surface gives a strong influence on D_s through a change in E_s. A decreasing coverage factor of H at higher T_s make the surface more reactive, causing an increase of E_s because a binding energy between SiH_x and adsorbing sites becomes stronger. Consequently, at higher T_s range, H elimination causes a decrease of D_s, which is a possible explanation for cryst.-to-amorphous transition at around T_s=500C.

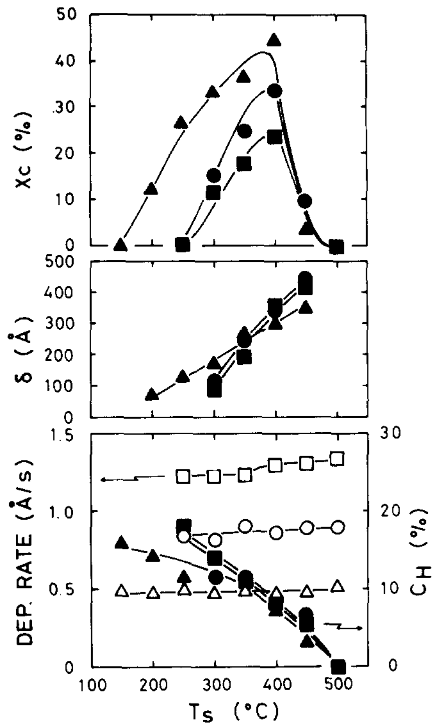

Fig.1. Volume fraction (X_c) and the size (δ) of microcrystallites, bonded H content (C_H) and the deposition rate of the films plotted against the substrate temperature (T_s).

Different from X_c, on the other hand, δ increases monotonously with T_s. Growth as well as coalescence of neighbouring μc nuclei is activated thermally at elevated temperatures. It should be noted that a decrease of H coverage on the surface at higher T_s enhances the coalescence of μc nuclei into a larger crystallite size through a reduction of hindrance effect of H.

3.2. Structure of the films from various plasma conditions

Figure 2 shows the structural characteristics of the deposited films (T_s=350C) mapped out on the RF power density / SiH_4-H_2 flow rate ratio plane, where a diameter of each three-quarter open circle represents δ and an area of each quarter solid circle X_c of crystallites in μc-Si:H. It is seen in the figure that δ becomes smaller with increasing RF power density in a whole SiH_4/H_2 ratio range. It should be noted that the structure of the film deposited via the glow discharge of pure (100%) SiH_4 stays microcrystalline when the flow rate is lowered to less than 0.4SCCM. It clearly indicates that H_2 dilution is not an essential condition for the formation of μc-Si:H. "A" in the figure represents "amorphous", namely, films deposited under these plasma conditions show disordered structure. It is clearly seen in the figure that there are a lower and an upper power density levels, by two of which the region for the formation of μc-Si:H is limited.

3.3. Correlation between the results of OES and the film structure

The deposition rate of a-Si:H from pure SiH_4 plasma is proportional to SiH^* emission (4127A) intensity over a wide-range plasma parameters as we reported earlier[12]. For the case of μc-Si:H deposition, the above proportionality is basically retained although some deviation is accompanied. It is partly because a large amount of H atoms exists in the present plasma.

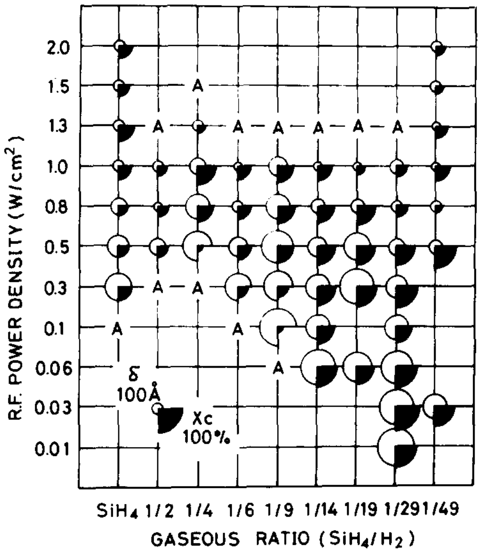

Fig.2. Crystallite size (δ) and volume % (X_c) of microcrystals in the deposited film mapped out on the RF power density / gaseous ratio plane.

Figure 3 shows the ratio of H^* emission (6563A) intensity in the plasma to the deposition rate (r) of resulting film plotted against RF power density for various SiH_4/H_2 flow-rate ratios. Open symbols in the figure represent amorphous phase while solid symbols microcrystalline. As shown in the figure, a film becomes amorphous when H^*/r ratio decreases down to less than a critical value, suggesting that the presence of some critical amount of H is required for μc formation depending on a growth time of monomolecular layer. In other words, a weaker H^* emission in the plasma means a lower H coverage factor on the growing surface, causing a decrease in D_s of SiH_x precursors, resulting in amorphous structure.

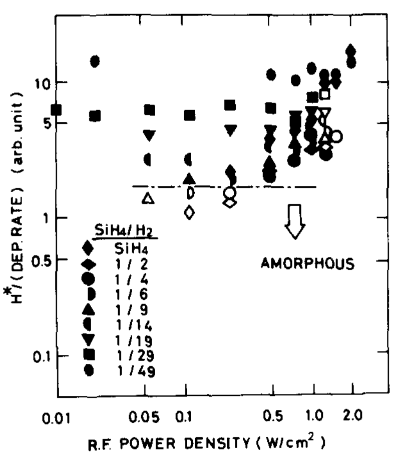

Fig.3. Ratio of H^* emission intensity in plasma to film dep. rate plotted against RF power density for glow-discharge plasma in various gaseous ratio.

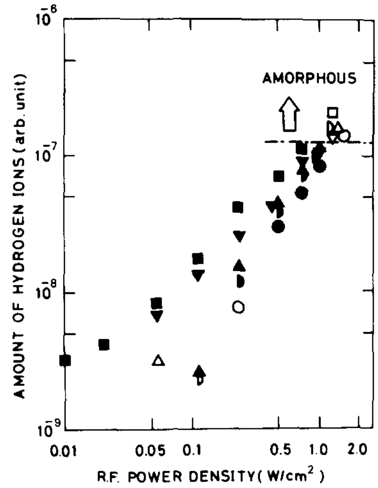

Fig.4. Relationship between RF power density and the amount of hydrogen ions impinging to the substrate surface in glow-discharge plasma for various gaseous ratio SiH_4/H_2. Marks used in the figure are the same as those in Fig.3.

3.4. Effect of ionic species on the growth of μc-Si:H

MS data provide an important information on the key factor for determining the upper RF power density level shown in Fig.2. Figure 4 shows the relationship between RF power density and the amount of hydrogen ions impinging to the substrate surface which were measured by MS through a fine orifice. As is seen in the figure, the structure of the deposited film becomes amorphous again when a total amount of hydrogen ions exceeds a critical value. It seems that ionic species reaching the substrate prevent the growth of μc nucleus.

Kinetic energy of impinging ions and their momentum transfer will be a possible model for crystalline-to-amorphous transition in the figure.

More detailed effects of ions impinging to the growing surface of μc-Si:H are shown in Fig.5; δ and $\Delta a/a_0$ as functions of the amount of impinging hydrogen ions. It indicates that δ is strongly affected by the amount of hydrogen ions impinging to the growing surface.

It should be noted that $\Delta a/a_0$ is not directly related with δ because $\Delta a/a_0$ comes to zero independent of δ when a flexible Al foil is used as the substrate material.

3.5. Crystallite size control in μc-Si:H

Taking into account the results mentioned in 3.4., δ has been intentionally controlled by varying the amount of impinging ions under a fixed plasma condition. For this purpose, the triode configuration was introduced in glow-discharge system where ionic species reaching the substrate is controlled by DC bias without giving any disturbance to plasma[13] as is sketched in the inset of Fig.6. Typical results are demonstrated in the figure. When the substrate bias is changed from -100V to +150V with fixed plasma condition (RF power density ; $0.5 W/cm^2$ and SiH_4/H_2; 1/9) δ is continuously and widely controlled.

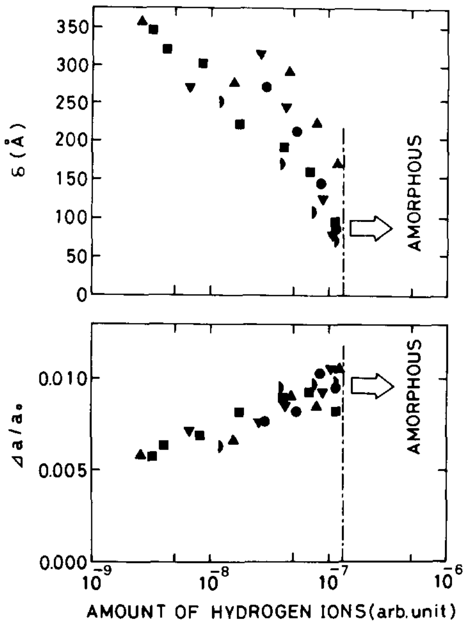

Fig.5. Crystallite size (δ) and relative lattice expansion ($\Delta a/ao$) of μc in resulting film plotted against the amount of hydrogen ions impinging to the growing surface.

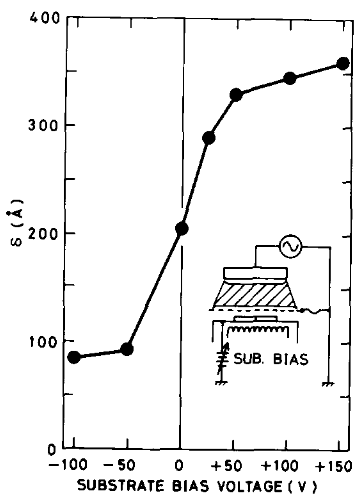

Fig.6. The demonstration of crystallite size control using the triode glow-discharge system.

3.6. Hall mobility of μc-Si:H

Electronic properties of μc-Si:H have been discussed by Spear et. al.[14] at the previous conference in the region of X_c exceeding 80%. In this report, dark-conductivity and Hall mobility were measured in various μc-Si:H in the range of 15-80% in X_c. Results are shown in Fig.7. The Hall mobility (μ_H) as well as the dark conductivity (σ_d) is well correlated with X_c although some statistical scatter exists. In this smaller X_c range than 80%, the magnitude of μ_H seems to be independent of δ.

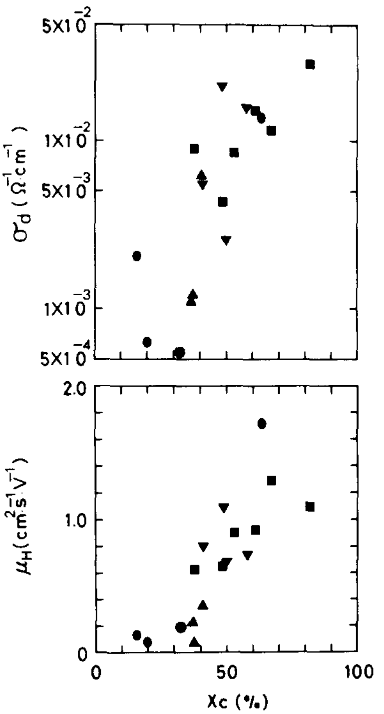

Fig.7. Dark-conductivity and Hall mobility of μc-Si:H films plotted against volume % (X_c) of μc.

4. SUMMARY

Formation kinetics of μc-Si:H from glow-discharge plasma has been discussed through the film growth under a variety of plasma conditions. RF power density, SiH_4/H_2 flow-rate ratio and the substrate temperature have been mainly scanned, and plasma diagnoses have also been performed.

(1) Surface diffusion coefficient D_s of the SiH_x admolecules should be large for μc nuclei formation; D_s depends both on temperature (T_s) and H coverage factor of the surface. Crystalline-to-amorphous transition at T_s higher than 500C originates from a decrease in D_s due to H-elimination reaction.

(2) Crystallite size δ increases as T_s increases, H coverage factor decreases and/or the amount of hydrogen ions in the plasma decreases.

(3) The role of hydrogen ions impinging to the growing surface is to cause lattice distortion and to reduce δ.

(4) Using the triode reaction chamber with DC bias, δ was continuously controlled in the range 90-360A by varying the amount of impinging ions.

(5) Hall mobility μ_H is mainly correlated with X_c rather than δ in the range X_c=15-80%.

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