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Nanocluster assisted fast rate epitaxy from Trichlorosilane under the mesoplasma condition

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Abstract: Mesoplasma CVD has been employed for direct production of wafer-equivalent quality silicon thin film solar cells as a next generation SIEMENS technology. Fundamental mechanism of epitaxial growth from trichlorosilane (TCS) as source gas is reasonably explained by the unique nano-cluster assisted deposition similar to the case with silane gas. One of the unique advantages of this process was in that epitaxial deposition rate increases with the input RF powers at a fixed TCS gas, claiming the high material yield as high as 60% at the power of 29kW, while the defect density decreases and the film quality is improved.

Keywords: mesoplasma, epitaxy, silicon, SIEMENS, molecular dynamics

1. Introduction

It is expected that single crystalline silicon thin films would be the ideal active layer due to its stability and high conversion efficiency associated with less carrier recombination center at reduced grain boundaries [1]. Such a ”wafer-equivalent single crystalline thin solar cells” may become available if quite fast high epitaxial film deposition and appropriate lift-off layer transfer to low cost foreign substrates are both to be established. In particular, a high deposition rate will be the technical requisite as the film thickness of at least 5 μm is required for crystalline Si thin film solar cells to cope with its indirect band gap characteristics.

Thermal chemical vapor deposition at atmospheric pressure using trichlorosilane ($SiHCl_3$: TCS) as a source gas is somewhat established major approach, known as a part of SIEMENS process. This process is essentially controlled by surface reaction of the equilibrium gas chemistries. As a result, the production yield is inevitably hindered by a formation of stable by-product silicon tetrachloride ($SiCl_4$: STC), resulting in as much as 30%, even if the growth rate is attained at ~ 100 nm/s at temperature ~1,100˚C [2].

Meanwhile, the equilibrium calculation of chemistries in the TCS system under the mesoplasma condition in the pressure range of 0.1~10Torr has indicated that the Si-containing chloride phases are no longer stable at temperatures higher than 2,000K and the Si(g) phase becomes the most stable phase instead [3]. One can foresee from this fact that high material yield would be attainable if this high temperature gas chemistries are frozen-in during epitaxial deposition, that is, the degree of non-equilibrium could be associated with the improvement of the material yield. In this aspect, mesoplasma CVD would be essentially advantageous as its fundamental deposition mechanism is based in the quenching of high temperature vapor to form clusters as growth precursors [4]. In fact, we have demonstrated high rate epitaxial Si film deposition and also the significant increase in the deposition rate with high input RF powers from SiH_4 as a source gas [5]. In addition to this potential advantage in the chemistries, the rapid quenching of high temperture gas mixture is important in affecting the chracteristics of nanoclusters as the actual growth precursor for the epitaxial film. It was suggested experimentally that 2~3 nm sized globular and loosely bound clusters are potentially formed when epitaxial films were deposited. In contrast, relatively large clusters formed at low power condition could result in the polycrystalline film formation [6]. Molecular dynamics (MD) studies have suggested supportively the role of such clusters as growth precursor in the epitaxial deposition process, and pointed out that the instantaneous cluster deformation and the spontaneous alignment of the comprising Si atoms upon impact is the fundamental mechanism of the cluster assisted fast rate epitaxy [7].

Taking account of these, higher input power condition seems to be prefereable for freeze-in the high temperature chemistries and thus supression of the stable chloride phase formation, as high temperature plasma flame extends towards substrate, and for cluster chracteristics for epitaxy, i.e., instantaneous and spontaneous atom ordering. These thus potentially facilitate simultaneous attainment of fast rate eptaixy, improved material yield and better film quality at the same time. With these as background, in this work, we attempt MD simulation to elucidate more detailed cluster role in the epitaxial growth espeically in the presence of hydrogen, and also the fundamental quality of the epitaxial Si films deposited at different input RF power conditions.

2. MD simulation of Si:H cluster dynamics as growth precursor

MD simulation for the Si cluster formation and the interaction between cluster and Si(100) substrate was carried out with the Tersoff potential. The detail of the calculation methodology can be found elsewhere [7,8]. Initially, a certain amount of Si and H atoms were placed in a MD cell of 100 x 100 x 100 Å^3, and heated up immediately to 1.78 of melting point of Si (T_m), at which all the atoms are confirmed at random as a vapor phase in advance. It was then cooled down to 0.18 T_m continuously at a rate in the order of 10^{12} K/s, and the clustering of atoms was confirmed at a certain temperature during cooling. The formed Si cluster that consists of *n* Si atoms is denoted hereafter as Si_n.

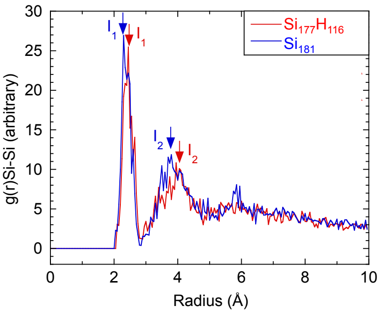

Fig. 1 Radial distribution function of $Si_{177}H_{116}$ and Si_{181} clusters observed during cooling process.

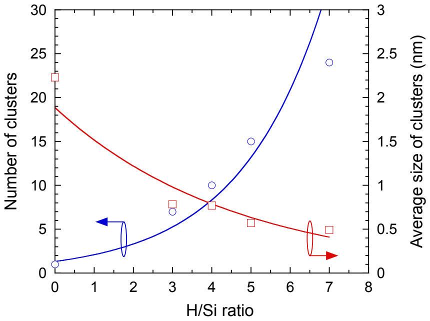

Fig. 2 Change in the number and the average size of the clusters created with different initial H/Si ratio.

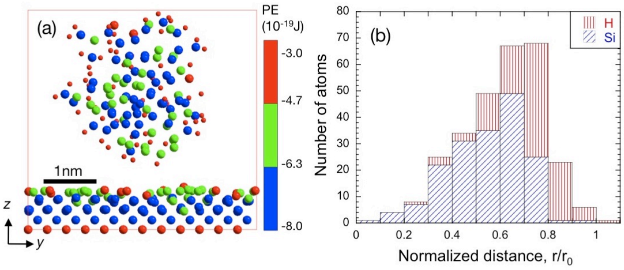

Fig. 3 (a) Distribution of atoms in a $Si_{177}H_{116}$ cluster (~2.3nm) with potential representation (large particle: Si, small particle: H atom), and the histogram of atom as a function of the normalized distance from the center of the cluster.

Similar to the case of Si cluster, the nano-sized globular Si:H clusters with liquid-like structure were found to form during rapid cooling of high temperature Si and H_2 vapor mixtures. From the radial distribution function (RDF) of $Si_{177}H_{116}$ cluster shown in Fig. 1, the local structure is quite similar to the liquid-like Si_{181} cluster under the same conditions. However, it is interesting to note that the number of the smaller clusters increases as the initial H/Si ratio increases as is seen from Fig. 2, suggesting that hydrogen atom tends to crack down the Si clusters.

Figure 3 shows the distribution of atoms in a potential representation (a) and the number of atoms at the relative position from the center of the cluster mass. It is seen that most of the H atoms are located near the surface of the clusters, but some are trapped within the clusters. Importantly, all these H atoms are relatively at higher potential compared to the Si atom.

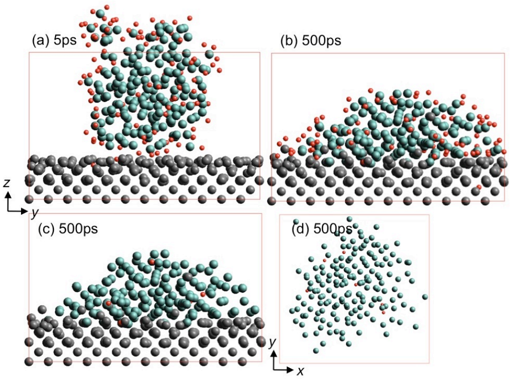

Fig. 4 Snapshots during deformation of $Si_{177}H_{116}$ cluster at the substrate temperature of 0.69 T_m; (a) before impingement, (b) 500 ps after impingement onto Si(100) substrate, (c) snapshot disappearing the H atoms at surface and (d) its top-view (projection in the XY plane).

The clusters shown in Fig. 3 were then used as the growth precursor for the cluster impingement simulation. Most importantly, no extra impact energy was applied to the cluster, as the growth precursor in the actual experiment was considered to arrive at a group velocity of several 10 m/s, which was somewhat 'soft-landed' on the surface. Therefore, the cluster falls downward to the substrate with the translational kinetic energy in the order of 10^{-3} eV/atom. Similar to the case of the Si cluster impingement, they exhibited instantaneous deformation and the comprising Si atoms were aligned to the crystal structure of the substrate spontaneously, as is seen from Fig. 4 (b). It is interesting to note that the degrees of deformation and alignment of the Si:H cluster is significant especially at low temperature, compared to those of the clusters with Si atoms only. Figure 4(c) shows the deformed cluster of Fig. 4(b) after making all the H atoms at the surface invisible, and its top view is shown in Fig. 4(d). These snapshots indicate that most of H atoms originally trapped within the cluster were not present within the deformed cluster. After the thorough observation during deformation, H atoms within the cluster were found to move toward the cluster surface individually and desorb as Si-H radicals during the deformation. It is therefore considered that the Si deformation dynamics would be promoted by the H atom movement in itself not by the local heat generation as a result of H atom recombination within the cluster.

3. Epitaxial film deposition

3.1 Experimental

Deposition experiments were carried out at fixed pressure of 6 Torr using the inductively coupled RF (13.56MHz) plasma generated with Ar and H_2 as plasma gases. Liquid TCS was heated to 40°C and gasified and then introduced into the reaction chamber as a gas phase. In order to suppress re-condensation of TCS and also to attain stable plasma generation with complete gas mixture (plasma blinks at low TCS flow condition), TCS gas and H_2 gas were mixed together before introduction to the reaction chamber. Also these gas mixtures were injected through the probe that was immersed into the plasma at the center of the ICP tube torch, as it resulted in more uniform deposition and higher material yields compared to the injection with the radial Ar gas from the periphery of the tube torch. The effect of TCS flow rate was investigated at a fixed power of 25 and 29 kW while varying the TCS flow rate from 20 to 150 sccm. The effect of input power was investigated from 23 to 29 kW at a fixed TCS flow rate of 100 sccm. The deposition time was fundamentally adjusted to attain a constant film thickness either 30μm or 50μm depending on the experiment, to avoid the effect of the defects that may depend on the film thickness.

As received non-doped Si wafer was cut into 2 cm× 2cm, cleaned with ultrasonic rinsing and placed on the water-cooled substrate holder positioned at a fixed distance (30 mm) form the torch exist. Substrate was subject to an instantaneous cleaning by mesoplasma for native oxides removal just before deposition. The typical deposition conditions are fundamentally the same with that for the epitaxial film deposition from SiH_4 that has been reported elsewhere [4].

The structure of the films was analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM), the surface structures were observed by AFM and nomarski microscopy. The thickness of the deposited films was measured by surface profiler and locally confirmed by the SEM observation. The carrier lifetime was measured by μ-PCD.

3.2 Effect of deposition time

Figure 5 shows the deposition time dependence of the thickness of deposited films and defect density on the surface of the deposited films. It is seen that the film thickness increases almost linearly with time. This suggests that the deposition is fundamentally at the steady state at least under the present condition examined. It is unfortunate, however, that the defects density at the surface increased with deposition time. From the Nomarski microscope observation, two distinct defects were detected, i.e., anisotropic square defects observed primarily for thinner films (<30μm) and isotropic round defects for thicker films (>30μm). From its size evolution tendency, anisotropic defect could be due to stacking fault originating from the initial growth surface, as a result of the unfavorable heterogeneous nucleation or contaminants on the substrate surface. In contrast, as no such isotropic defects were observed for the deposition with SiH_4 gas, these defects are considered to be associated with accumulation of Cl chemistries on growth surface. Nevertheless, it is clear that the defect formation does not affect the epitaxial growth itself.

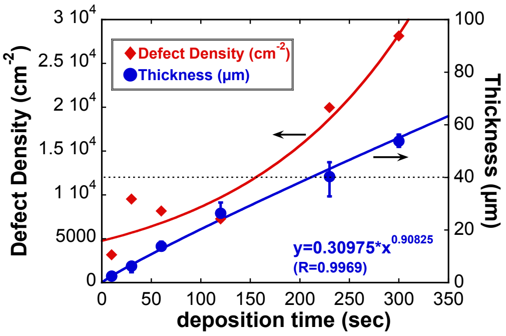

Fig. 5 Variation of the surface defect density and epitaxial film thickness with time. (TCS: 50sccm, RF Power: 29kW)

3.2 Effect of TCS

Figure 6 shows the changes of deposition rate and defect density with TCS flow rate at the two different input RF powers, 25 and 29kW. Thickness of all the films in this series is adjusted to be 50 μm. It is seen that the deposition rate is fundamentally increased with TCS flow rate. However, it shows gradual saturating tendency especially at high TCS flow rate for both different RF input powers. The defect density is also found to increase with TCS flow rate. As explained in 3.2, the defects in thick films are mostly isotropic and could be associated with Cl concentrations on growth surface. Therefore, i the epitaxial growth rate could be affected by the SiClx chloride formation on growing surface at the increased Cl partial pressures at high TCS flow rates.

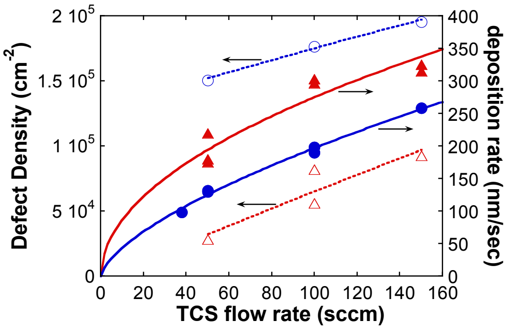

Fig. 6 Variation of surface defect density and deposition rate with TCS flow rate (sccm). Circle and triangle are for the case of 25 kW and 29 kW, respectively.

3.3 Effect of RF power

As already seen in Fig.6, the epitaxial deposition rate is increased at 29kW compared to that at 25kW. Such an increase in the deposition rate is evident from Fig. 7. Even at a fixed TCS flow rates of 50 sccm, the deposition rate at 23kW is nearly doubled to be 230 nm/s at 29kW. It is also important to note that the defect density decreases significantly with an increase in the RF power. The film thickness of this series is less than 30μm, indicating that the defects are mostly anisotropic originating from the surface of the substrate surface. Taking account of the cluster dynamics discussed in section 2, this may be due to the increased degree of the loosely bound cluster structure that would be more favorable for cluster deformation and self-ordering to attain better epitaxial relationship at the interface. Alternatively, exposure to high power Ar-H_2 plasma may more effectively clean the Si surface [9]. Although more detailed analysis is necessary to identify this mechanism, it is clear that high power condition is quite effective for both increase in the fast rate epitaxial deposition and improvement of the film quality at the same time.

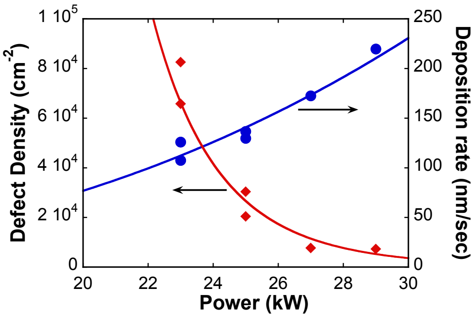

Fig. 7 Variation of surface defect density and deposition rate with input RF power. (TCS=50sccm, Dep.time=2min.)

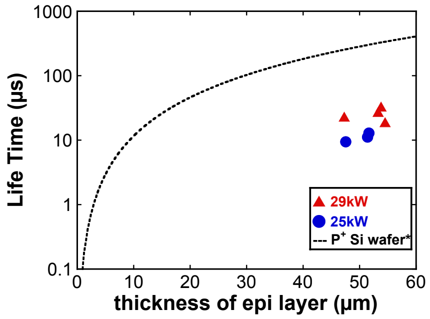

Fig. 8 Variation of carrier lifetime with thickness of epitaxial films deposited at different input RF powers, comparing with the thickness dependent typical Si wafer lifetime (dotted line).

Figure 8 shows that lifetime of the photo-induced carriers measured by μ-PCD for the films deposited at different input RF powers. It is seen that the lifetime for the films at 25kW is increased when deposited at 29kW. This actually demonstrates the effect of the higher power also for the improvement of the electric quality of the film. Although the highest lifetime attained in this series was only 50μs, it is reasonable for the films with no passivation layer applied.

For these films, the deposition efficiency was estimated to be 36 % at the input RF power of 25kW and ~ 60% at 29kW, assuming that the effective deposition area was the circle with ø 40 mm diameter (this estimation was cross checked by thickness uniformity measurement and also by weighing the total film deposited [10]). We observed that the plasma flame was extended toward the substrate at higher power conditions [10]. Therefore, the high temperature chemistries could be more effectively frozen-in and condensed to form nano-cluster growth precursors with reduced SiClx phase formation at higher power condition.

4. Conclusion

Silicon epitaxial films have been deposited from trichlorosilane by mesoplsama CVD. The fundamental growth mechanism is considered to be cluster assisted deposition which is fundamentally similar to that observed for the case of SiH_4. Although the epitaxial film deposition rate increases with TCS, the defect density is also increased, which is potentially associated with the increased Cl concentration. However, higher RF input power was found effective to increase the epitaxial deposition rate, i.e. the deposition efficiency, and also to decrease the defect density significantly at the same time. As a results, at 29kW, Si epitaxial films deposited at > 200nm/sec with the material deposition yield ~60% have shown the photo-induced carrier lifetime of ~50μs.

5. References

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