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Deposition mechanism of thin Si and Ge films promoted by liquid-phase reduction under ballistic hot electron incidence

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Abstract

The mechanism of liquid-phase thin film deposition based on ballistic electron incidence we reported previously is studied for Si and Ge. These thin films are deposited by direct incidence of ballistic electrons emitted from nano-crystalline Si (nc-Si) emitter into $SiCl_4$ and $GeCl_4$ solutions coated on the target substrate. The thermodynamic and mass-transport modeling of the sequential process through reduction, nucleation, and deposition can explain well the experimental observation by spectrometric characterizations that thin films grown on the substrate are composed of Si and Ge nanoclusters with no contaminations.

1. Introduction

Thin film deposition technology utilizing electron beams has been studied as a method for direct formation of nanostructures [1,2]. This method has some problems such as ultra-high vacuum, high acceleration voltage, complicated setup, and poor film quality of the obtained thin film. We have proposed a thin film deposition scheme utilizing electrons with high reducing activity emitted from nano-crystalline Si (nc-Si) ballistic hot electron emitter [3,4]. By irradiating ballistic electrons on the target substrate coated with salt solutions, a reduction reaction is induced in the solution and then a thin film is deposited with neither by-products nor contaminations on various substrates including insulators. To clarify the deposition process of this electron incidence mode, analyses of the reduction, nucleation, and the subsequent deposition are reported here. The result of modeling is discussed in relation to the experimental observations.

2. Experimental Procedure

A schematic illustration of the printing method is shown in Fig. 1. The all thin-film deposition was carried out in a N_2 filled glove box. The nc-Si ballistic electron emitters were fabricated by anodization of poly-Si on n^+-Si wafers [3,4]. First, nc-Si emitter was located with a small gap in front of a Cu target substrate coated with a 0.5 M $SiCl_4$ or a 0.5 M $GeCl_4$ propylene carbonate solution using a piezoelectric actuator. Subsequently, the inside of the glove box was depressurized in consideration of the vapor pressure of the coated solution (10–10^3 Pa), and then the emitter was pulse driven. The gap distance between the emitter and the target substrate was determined from the pressure dependence of the mean free path of ballistic electrons (50 µm–5 mm). After the emitter operation, the residual solution was removed by elution or evaporation. The deposited films were characterized by scanning electron microscope (SEM), energy dispersive X-ray (EDX), and X-ray photoelectron spectroscopy (XPS) measurements.

3. Results and Discussion

When ballistic electrons were irradiated to a Cu substrate coated with a $SiCl_4$ solution, a thin film was deposited on the Cu substrate surface. As a result of EDX analysis, characteristic X-ray signal of Si was confirmed, indicating that thin Si film was deposited by ballistic electron irradiation. In the EDX spectra, there are no Cl signals, and thus it seems that ballistic electrons preferentially reduced the Si^{4+} ions in the solution followed by thin film growth. This deposition effect was also confirmed by XPS measurements. The wide-scanned XPS spectrum of the deposited thin Si film is shown in Fig. 2. Since no Cl signal was also detected from this XPS spectrum, it is suggested that Cl contamination level in the deposited film is suppressed to 300 ppm or less. Similar results were obtained with printing deposition of thin Ge film. In addition, it has been clarified by XPS and Raman measurements that deposited films consist of very small nano-clusters, as reported in previous our study [4].

Based on the experimental results, a simple deposition model is provided. As shown in Fig. 1, positive ions in the vicinity of penetration depth of ballistic electrons into the solution are promptly reduced followed by nano-cluster formation. The generated nano-clusters migrate to the target substrate by diffusion. In order to verify this model, we estimated the free energy of a cluster formation ΔG for Si and Ge, as a function of incident electron energy on a basis of thermodynamic nucleation analysis [4]. The inset of Fig. 3 shows the relationship between the free energy of a Si cluster and the radius of the cluster, r, at the irradiation electron energy of 2.5 eV. The positive and negative values of ΔG represent the diffusion and nucleation of a cluster, respectively. It can be seen how the curve reaches a maximum, $\Delta G_{\max}$, which represents the energetic barrier that needs to be surpassed to achieve nucleation. Figure 3 plots $\Delta G_{\max}$ values of Si and Ge clusters as a function of the incident electron energy. The smaller $\Delta G_{\max}$ the easier nucleation proceeds, since the transfer of ions from solution to the crystal phase becomes dominant over the increase of surface energy. At the electron energy of 10 eV, the $\Delta G_{\max}$ of Si and

Ge clusters are almost the same, but in the vicinity of 4 eV, the ΔG_{max} of Ge is smaller than that of Si. Indeed, it was confirmed that a Ge-rich film with a composition ratio of Si:Ge≃0.3:0.7 was formed by irradiating ballistic electrons with an energy of 4 eV to a mixture solution of SiC_4+$GeCl_4$ (1:1 in volume ratio).

Our modeling is further supported by mass transfer analysis of generated nano-clusters in solutions. The generation and diffusion of clusters can be represented by one-dimensional reaction-diffusion equation [5],

$$\frac{\partial[X]}{\partial t} = D\frac{\partial^2[X]}{\partial x^2} + \frac{1}{\sigma(r)}\frac{J_e}{nF}\delta(x-\lambda) \qquad (1)$$

where $[X]$ is the concentration of the diffusing clusters at location x and time t, D is the diffusion coefficient, J_e is the emission current density, n is the valence of the ion, F is the Faraday constant, λ is the penetration depth of incidence electrons, $\sigma(r)$ is number of atoms in a cluster, and $\delta(x)$ is Dirac delta function. The first term on the right side corresponds to the diffusion term, and the second term to the generation rate of the cluster. It is assumed that when the ballistic electrons are irradiated, the clusters are promptly generated at λ, as shown in Fig. 1. The spatial distributions of Si nanoclusters at each time calculated based on Equation (1) under semi-infinite boundary conditions are shown in Fig. 4. The cluster concentrations are uniformly distributed over 1 μm at >0.1 s. Since the thickness of the coated solution in our experiment is about 100 nm, the results mean that generated clusters easily propagate to a target substrate. Similar results were obtained from Ge clusters.

4. Conclusions

The reducing activity of ballistic electrons emitted from nc-Si diode is useful for depositing thin Si and Ge films under a direct incidence into salt solutions coated on the target substrate. No significant contaminations are detected in deposited thin films. Analyses based on the nucleation theory and reaction-diffusion scheme showed that ballistic electrons injected into solutions quickly reduce positive ions in the range of the penetration depth therein to form nano-clusters, and then diffuse to the target substrate within a short time. It is expected that this printing approach potentially useful for a clean, low-temperature, damage-less, and power-effective deposition process.

References

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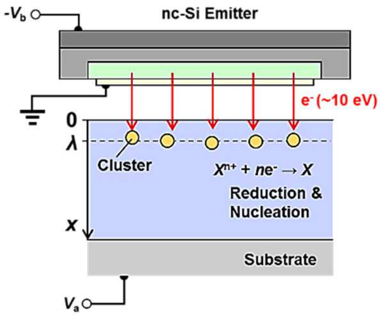

Fig. 1 Schematic illustration of thin film deposition under a ballistic electron printing scheme.

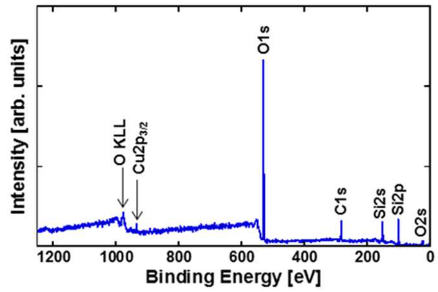

Fig. 2 Wide-scanned XPS spectrum of deposited thin Si films. Cl contamination is not detected.

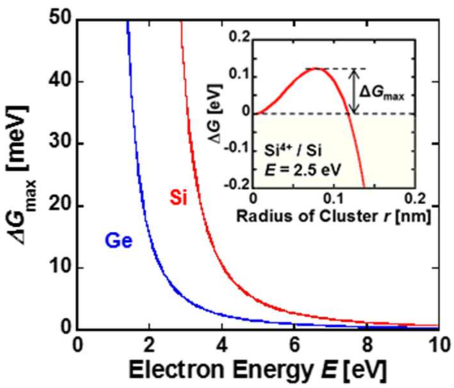

Fig. 3 ΔG_{Peak} of Si and Ge clusters as a function of electron incidence energy. Relation between ΔG_{max} of Si and cluster radius r at electron incidence energy of 2.5 eV is shown in the inset.

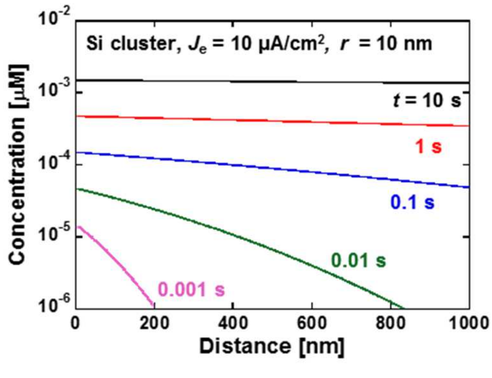

Fig. 4 Spatial distribution of Si clusters at each time.