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Criterion for Ballistic-electron Printing of Thin Metal and Group IV Films

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Abstract

The usefulness of the reducing activity of ballistic hot electrons emitted from a nanocrystalline silicon (nc-Si) diode has been demonstrated under a printing scheme of thin-film deposition. Emitted ballistic hot electrons impinge upon a solution-coated substrate that is located in proximity close to the emitter. It is shown from spectroscopic characterizations that thin Cu, Si, and Ge films are deposited onto the target substrate. Analyses of ballistic electron effects suggest that there is a critical energy for promoting preferential reduction of target ions within the penetration depth in solutions followed by the nuclei formation for the growth of thin films.

1. Introduction

To meet the increasing demands for the advanced device structures and substrates, the development of clean, low-temperature, damage-less, and power-effective thin-film deposition process has been required. One possible approach is to use the highly reducing activity of ballistic hot electrons emitted from a nanocrystalline silicon (nc-Si) diode. When the nc-Si emitter is operated in salt solutions, output electrons leads to deposition of thin metal and semiconductor films on the emitting area [1-3]. Based on these results, electron printing scheme was developed, in which a solution-coated target substrate is located in close proximity to the emitter. When Cu salt solution coated substrates are irradiated with emitted electrons, reductive reaction of Cu^{2+} ions efficiently proceeds followed by the growth of thin Cu films [4]. Here we report the results of expansion of the printing mode to deposition of thin Si and Ge films. Key factor for the nuclei formation in this process is discussed by modeling the effect of ballistic electron incidence.

2. Experimental Procedure

The nc-Si emitter is a kind of metal-insulator-semiconductor (MIS) diode consisting of a thin film surface electrode, an electrochemically anodized nc-Si layer (~1.6 μm thick), a crystalline silicon (c-Si) wafer substrate, and a back contact. The emitter was prepared as described previously [1-4]. The experimental configuration of the printing scheme is shown in Fig. 1. At first, a $CuCl_2$ $SiCl_4$, or $GeCl_4$ solution was spin- coated (100 nm in thickness) on a substrate (e.g., Si wafer, thermally grown SiO_2/Si, or Cu). This substrate was located in front of the nc-Si emitter. A gap between them was appropriately controlled by a piezoelectric actuator, taking the ambient pressure dependence of ballistic hot electrons' mean free path into account. For thin film deposition, the nc-Si emitter was driven in an intermittent pulse at V_b = 10-18 V with a duty ratio of 20%. The voltage V_a between the emitter and the substrate was 0-20 V. A series of experiments were carried out in a N_2 gas filled glove box. After the processing, residual solutions were removed by dissolving into solvents. The structure and chemical composition of the deposited thin films were characterized by scanning electron microscopy (SEM), energy dispersive X-ray (EDX) measurements, atomic-force microscope (AFM), and spectroscopic reflectometer.

3. Results and Discussion

For thin film deposition, the nc-Si electron emitter is driven in an intermittent pulse at V_b = 10-18 V with a duty ratio of 20% for several tens of minutes. After the operation, a color change appeared in the target substrate, due to the growth of a thin film. Figure 2 shows the SEM image of the deposited thin Cu film near the boundary of the original c-Si area. We can see that after removing residual aqueous solution of $CuCl_2$, the thin Cu film is deposited on the impinging area. The EDX spectra and the corresponding SEM images obtained from original c-Si and deposited thin film surfaces suggest the high compositional and structural uniformity of the deposited film, as shown in Fig. 2. The characteristic X-ray signals of Cu corresponding to Lα, Kα, and Kβ were clearly detected with no contaminations such as C and Cl. Obviously, this as-deposited thin film is composed of pure Cu. The results indicate that impinging energetic electrons preferentially reduce Cu^{2+} ions at the solution surface followed by the nucleation for the growth of thin Cu films. It has been confirmed that the printing scheme is also available for oxidized Si substrates.

On the basis of the results mentioned above, this technique was applied to the deposition of a thin Si film using a $SiCl_4$-dissolved propylene carbonate coated on Cu substrate. The EDX spectrum and the corresponding SEM image obtained from a deposited thin film are shown in Fig. 3. The characteristic X-ray signals of Si were clearly detected. The energy peak corresponding to the O (Kα) is due to natural oxidation during the exposure to air before the EDX measurement. The peak of Cl (Kα) is likely due to the solution residue. This component might be removed by complete dissolution treatments. Actually, in case of the Cu printing, no contamination signals were detected in EDX spectra after a sufficient dissolving process. Similar thin-film deposition was obtained from $GeCl_4$ solution.

In the printing scheme, unilateral reduction occurs in solutions differently from the exchange of thermalized electrons in the conventional electrode reaction. Due to a fast reduction kinetics under electron incidence with a mean energy of 10 eV at J_e = 10~100 μA/cm^2, a significantly large number of cluster is generated at an electron penetration depth (about 10 nm) as indicated in Fig. 4(a). To clarify the triggering factor of nucleation, we estimated the free energy of a cluster formation, ΔG, as a function of incident electron energy on a basis of thermodynamic nucleation analysis [5]. Figure 4(b) shows calculated ΔG vs. R curve for Cu at different electron energies, where R is the radius of Cu cluster. The result suggests that electron energy of 10 eV is suitable for promoting the growth of Cu clusters followed by the formation of a sort of atomic nano-sheet. Similar behavior has been confirmed by analyses for the either case of Si or Ge. Electron energy in this case corresponds to an effective external applied potential in the conventional electroplating ("electrochemical window" + "over-potential"). The nc-Si emitter meets well the requirement for this criterion.

4. Conclusions

Alternative scheme for thin-film deposition was proposed using ballistic hot electrons as a printing beam. When metal- or semiconductor-salt solution coated target substrates are irradiated with emitted electrons, reduction of positive ions efficiently proceeds followed by the growth of thin films. The electron incidence at energy of 10 eV is a critical factor for triggering the cluster formation.

References

[1] N. Koshida, T. Ohta, B. Gelloz, and A. Kojima, Current Opinion in Solid State and Mater. Sci. **15**, 183 (2011).

[2] T. Ohta, B. Gelloz, and N. Koshida, Appl. Phys. Lett. **102**, 022107 (2013).

[3] R. Suda, M. Yagi, A. Kojima, R. Mentek, N. Mori, J. Shirakashi, and N. Koshida, Jpn. J. Appl. Phys. **54**, 04DH11 (2015).

[4] R. Suda, M. Yagi, A. Kojima, N. Mori, J. Shirakashi, and N. Koshida, J. Electrochem. Soc. **163**(6), E162 (2016).

[5] M. Paunovic and M. Schlesinger, *Fundamentals of Electrochemical Deposition, 2nd ed.* (John Wiley & Sons, New York, 2006).

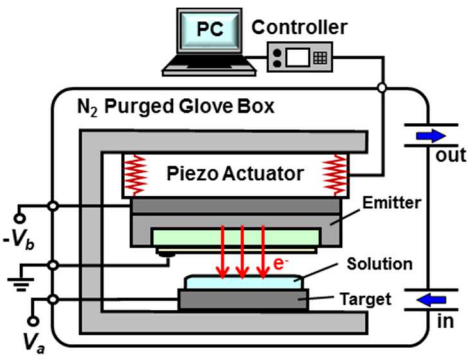

Fig. 1 Schematic experimental configuration of thin film deposition under a ballistic electron printing scheme.

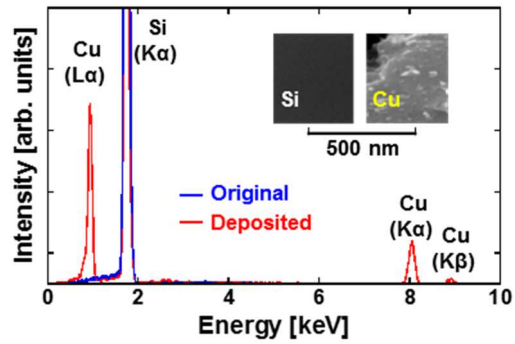

Fig. 2 The measured EDX spectra of the original and deposited substrate surfaces. The SEM image near the boundary between the original c-Si and deposited thin Cu film is also shown in the inset.

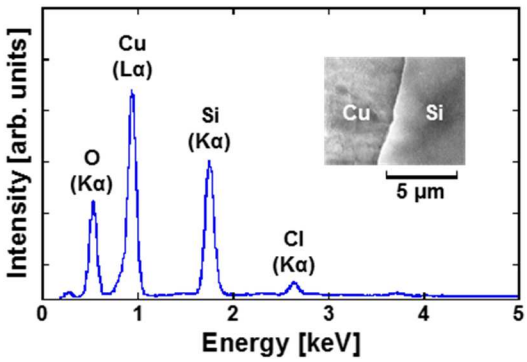

Fig. 3 The measured EDX spectrum of a Si film deposited on a Cu substrate under a printing mode. The SEM image near the boundary between the original Cu substrate and deposited thin Si film is also shown in the inset.

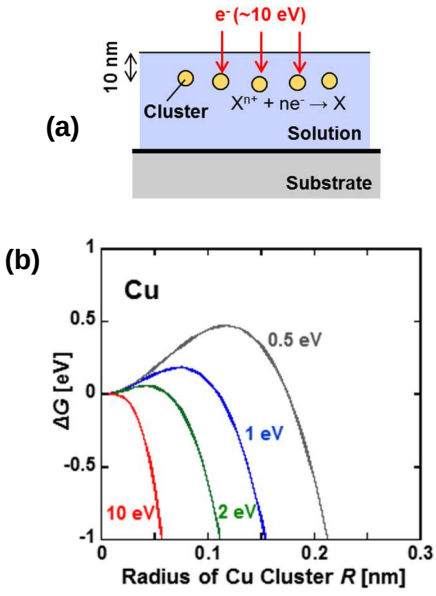

Fig. 4 (a) Schematic illustration of the electron-induced reduction at the penetration depth leading to nucleation in the printing scheme. (b) Free energy of formation of a Cu cluster as a function of cluster radius at different electron incidence energies.