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Deposition of Thin Si, Ge, and SiGe Films by Ballistic Hot Electron Reduction

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Abstract

Liquid-phase deposition scheme of thin group-IV films is presented under ballistic hot electron injection into solutions. Energetic electrons emitted from nanocrystalline Si diode reduce target ions at the interface followed by the deposition of thin amorphous Si, Ge, and SiGe films with no contaminations.

1. Introduction

When a nanocrystalline silicon (nc-Si) surface-emitting ballistic electron source [1] is driven alone in salt solutions, energetic hot electrons are supplied into the solid-solution interface followed by the reduction of positive ions, and then thin metal and semiconducting films are deposited on the emitting area [2]. In the case of $SiCl_4$ solutions, thin amorphous Si films are uniformly deposited with neither by-products nor contaminations [3,4]. In addition to Si, the usefulness of this low-temperature wet mode as a high-versatility process is demonstrated here for depositing thin Ge and SiGe films, along with their structural and compositional characterizations.

2. Experimental section

The nc-Si planar cold cathode is composed of a thin Au/Ti film (10 nm/1 nm), an nc-Si layer, n^+-Si substrate, and a back contact. As described previously [1,2], the nc-Si layer was formed by a constant-current anodization in an ethanoic HF solution followed by the electrochemical oxidation and subsequent super-critical drying (SCRD) treatments such that the nc-Si dot chain are interconnected with high-quality tunnel oxides.

For the thin film deposition, a simple experimental configuration was employed here as shown in Fig. 1, in which a very small amount of solutions (a few μl in volume) of $SiCl_4$ or $GeCl_4$ was dripped onto the limited emitter surface area using a controlled dispenser system, and then the nc-Si electron emitter is driven at a certain applied voltage V_b=10~15 V without using any counter electrodes. The deposition of thin SiGe films was also carried out in a mixture solution of $SiCl_4$+$GeCl_4$ (1:1 in volume ratio). As in the case of $SiCl_4$ and $GeCl_4$, the electrochemical effect of the electron emission was analyzed by cyclic voltammogram measurement in $SiCl_4$+$GeCl_4$ solutions separately under a standard three-electrode system. All the experiments were done in a N_2 gas filled glove box.

The structure and chemical composition of deposited thin films were characterized by scanning electron microscope (SEM), energy dispersive X-ray (EDX) measurements, atomic-force microscope (AFM), cross-sectional transmission electron microscopy (TEM), electron diffraction, X-ray photoelectron spectroscopy (XPS), and secondary ions mass spectroscopy (SIMS).

3. Results and discussion

After operating the nc-Si device for a few minutes under the situation of Fig. 1, thin films deposition on the emitting area was observed in every solution. The result of cyclic voltammogram measurements in a $SiCl_4$+$GeCl_4$ solution under a standard three-electrode configuration clearly shows that the ionic conduction in the solution is activated under the operation of the nc-Si emitter, and that the anode current is significantly increased even in the potential range within the electrochemical window of the solution as in the $SiCl_4$ or $GeCl_4$ solution case. Obviously ballistic hot electrons emitted through the thin surface electrode of the nc-Si emitter promotes the reduction of Si^{4+} and Ge^{4+} ions at the surface-solution interface leading to the atom migration and subsequent nuclei formation for the film growth.

Figures 2(a) shows a SEM micrograph of a deposited thin Ge film near the boundary of the emission area. It can be seen that a thin compact Ge film is deposited uniformly. The corresponding XPS spectrum is shown in Fig. 2(b). The signal of Ge is observed with signs of natural oxidation. No contamination signal of Cl is detected. It looks that the unilateral reduction proceeds at the emitting surface with no byproducts. Further evidence of this deposition model is obtained from the SIMS measurement for a deposited thin Ge film (Fig. 3). The Ge signal intensity profile peaks properly in the surface region with no significant contaminations.

Similar results were obtained from $SiCl_4$+$GeCl_4$ solutions as well. The SEM micrograph and the XPS spectra of a deposited SiGe film are shown in Fig. 4(a) and Fig. 4(b)-(c), respectively. The contaminations are below the detection limit of XPS, as in the case of Si and Ge. The compositional ratio estimated from the SIMS profile was $Si_{0.9}Ge_{0.1}$. This ratio might be controlled by changing the initial mixture ratio of $SiCl_4$+$GeCl_4$.

4. Conclusion

It has been shown that the injection of ballistic hot electrons into dripped solutions produces uniform deposition of thin amorphous group-IV films. This mode is triggered by preferential reduction of target ions with no byproducts. Besides elemental semiconductors (Si and Ge), thin SiGe films can also be deposited. In contrast to the conventional dry process based on the decomposition of active gases, the ballistic electro-reduction proceeds at room temperature. This phenomenon is potentially useful as a sequential process for fabrication of multilayered nanostructures and thin film devices.

Acknowledgements

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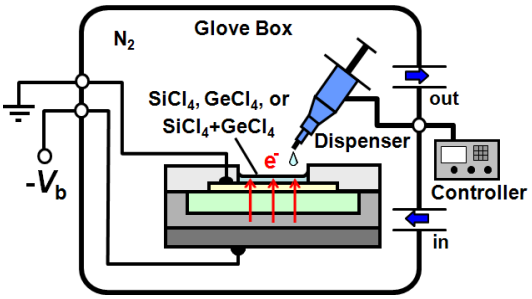

· Fig. 1. Schematic configuration for deposition of thin Si, Ge, or SiGe film by ballistic hot electron injection into solutions. A very small amount of solution was dripped onto the emitting surface regulated by a barrier mask. Note that no counter electrodes are used.

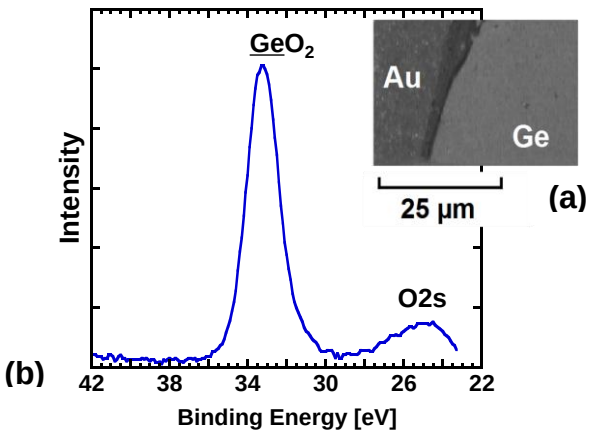

Fig. 2. SEM micrograph (a) and XPS spectrum (b) of a deposited thin Ge film.

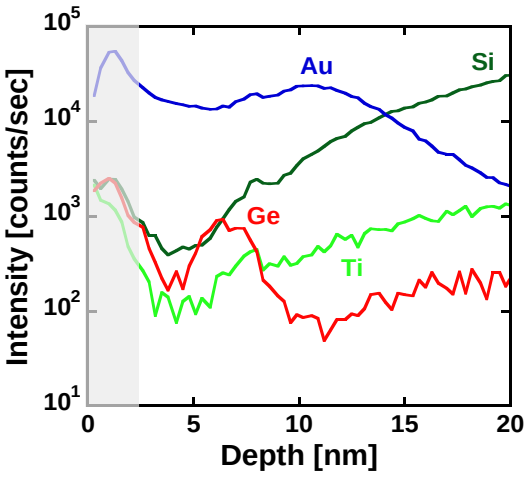

Fig. 3. Measured SIMS profile of a thin Ge film deposited on the emitter surface..

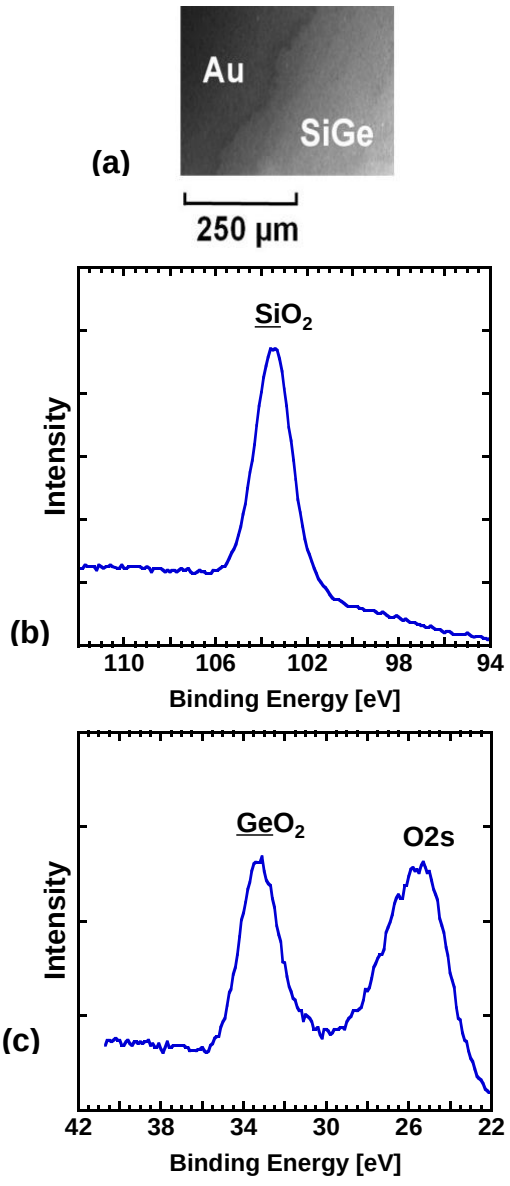

Fig. 4. SEM micrograph (a) and XPS spectra (b, c) of a deposited thin SiGe film.