Synthesis and Characterization of Clusters Assembled Films Composed of Transition-Metal Encapsulating Si Clusters

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Introduction
Hydrogenated amorphous Si (a-Si:H) is a semiconductor material useful to a wide range of applications, e.g., thin film transistors and solar cells etc. Properties of a-Si:H strongly depend on the structural and electronic disorders controlled by the hydrogen termination of dangling bonds[1]. As an alternative way to compose Si-based semiconductor films, here we propose a novel method of material synthesis; i.e. formation and deposition of transition metal (M) encapsulating Si clusters MSiₙ (n = 8-16)[2].

The MSiₙ clusters are stabilized by covalent bonds between the central M atom and the surrounding Si atoms (Fig. 1)[3], and have a large gap between the highest occupied molecular orbital and the lowest unoccupied molecular orbital (HOMO-LUMO gap: E_HL) for specific combinations of the M species and n values, e.g., 2.14 eV for MoSi₁₂. Reflecting the large E_HL, clusters-assembled films of the MSiₙ are expected to be semiconductor materials. In fact, the atomically thin layered film (MoSi₁₂), was predicted to be a semiconductor with an energy band gap ~0.8 eV by ab initio calculations[4].

In this paper, we demonstrate synthesis of MSiₙ (M = Mo, Nb and W, n = 1-16) assembled films and discuss their structural, optical and electrical properties using microscopic Raman scattering spectroscopy, X-ray absorption spectroscopy (XAS), X-ray photoelectron spectroscopy (XPS), optical-absorption spectroscopy and Hall measurements.

Preparation of MSiₙ cluster assembled films
The MSiₙ cluster films were synthesized by deposition of hydrogenated MSiₙ (MSiₙHₓ) clusters onto silica substrates at room temperature (RT) followed by annealing at ~500°C for 10 minutes in a ultra high vacuum for dehydrogenation. The MSiₙHₓ clusters were synthesized by reaction between SiH₄ molecules and M atoms supplied by laser ablation. The laser pulses were focused onto M targets in a silane SiH₄ pressure of 3-20 Pa. We measured compositions of the MSiₙ films using Rutherford back scattering and XPS. Compositions of the MSiₙ films were controlled by the SiH₄ pressure. In the film, the MSiₙ clusters were not crystallized but randomly connected with each other.

Results and Discussion
Figure 2 shows Raman scattering spectra of MoSi₁₂ and NbSi₁₃ cluster films and an a-Si:H film as a reference. We found a similar TO phonon band near 470-480 cm⁻¹ for the cluster films and the a-Si:H film. This indicates that similar amorphous Si (a-Si) networks are formed in the cluster films. However, the a-Si networks did not include Si-H bonds, because Si-H vibrations of 2000-2200 cm⁻¹ were not observed in the cluster films. Figure 3 shows XPS spectra of Si 2p and Nb 3d from the NbSi₁₃ cluster film before and after air exposure. After the air expose, the oxidation of Si was observed, while no chemical shift was found in the Nb 3d peaks. In other words, the Nb atoms were not oxidized by the air exposure. This indicates that Nb atoms are encapsulated in Si networks in the NbSi₁₃ cluster film. To identify local structure, we measured XAS for the WSiₙ (n~10) films. Results of the XANES and EXAFS of the W L₃ adsorption edge show that i) the W atom is surrounded by approximately ten Si atoms, and ii) the W-Si distance is distributed in a narrow range of 0.253-0.258 nm. These results indicate that the WSi₁₀ film actually consists of WSi₁₀ clusters. To investigate the electronic structure of MSiₙ cluster films, we measured optical-absorption spectra. The optical gap E_ΟH of ~1 eV was observed for WSi₁₀ and MoSi₁₂ cluster films by estimation using the Tauc plot as shown in Fig. 4. Figure 5 shows variation of E_ΟH values depending on the n value. When the n value reaches 5, we found the rise of E_ΟH, indicating that MSiₙ (n ≤ 5) cluster films have a semiconducting energy gap. The E_ΟH increases with increase of n and reaches ~1 eV for n~10 reflecting the large E_HL gap of the free MSiₙ clusters.

As shown in Fig. 6, electrical resistivity ρ of the MSiₙ films at RT increased exponentially from 0.001 Ωcm to 10 Ωcm range with increase of n. When the n value reaches ~10, ρ shows semiconductor range values of 1-10 Ωcm. This reflects the increase of the energy gap of MSiₙ (n~10) cluster films mentioned above. We measured temperature dependence of conductivity σ (= 1/ρ ) for MoSiₙ (n = 5, 9, 12 and 16) cluster films (Fig. 7). The σ increased with decrease of the substrate temperature. This indicates that the MoSiₙ cluster films have a semiconducting transport...
property. Activation energies $E_a$ of $\sigma$ were calculated from the 1/17 curves in Fig. 7 as 0.02 - 0.12 eV, confirming the gap opening as the $n$ value increases. However, the $E_a$ values are much smaller than the $E_{bg}$ in Fig. 5. This suggests that the carrier transport is supported by gap states arising probably from defects in the cluster films.

We found superior transport properties in Hall measurements of the MoSi$_n$ cluster films. The MoSi$_8$ and MoSi$_{12}$ films are p-type semiconductors with a mobility of 13 and 32 cm$^2$/Vs at RT, while usually the p-type a-Si:H has the mobility less than 0.1 cm$^2$/Vs[5]. The high mobility is due to reduction of electronic disorders of a-Si networks by using MoSi$_n$ clusters as a building block of the films.

Conclusions

In conclusion, the $M$Si$_n$ ($M=$ Mo, Nb and W) cluster assembled films are synthesized by the deposition of MoSi$_n$ clusters onto solid substrates followed by thermal annealing at $\sim$500°C. The resulting Si network in the film is similar to the a-Si network, in which the M atom is encapsulated. When the $n$ value is $\sim$10, the MoSi$_n$ cluster film is a semiconductor with the gap of $\sim$1 eV. The MoSi$_n$ ($n=$8, 12) films are p-type semiconductors and have the mobility higher than 10 cm$^2$/Vs. Thus, the MoSi$_n$ cluster film will be an attractive material for thin film devices.

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References