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

Noriyuki Uchida[1], Hiroshi Kintou [1], Yusuke Matsushita[1], Tetsuya Tada[1], Kazuhiro Kirihara[2], Hiroyuki Oyanagi[3] and Toshihiko Kanayama[1]

[1] Nanodevice Innovation Research Center, National Institute of Advanced Industrial Science and Technology, Japan
1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan
Phone: +81-29-849-1636 E-mail: nori-uchida@aist.go.jp
[2] Nanotechnology Research Institute, National Institute of Advanced Industrial Science and Technology, Japan
1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan
[3] Photonics Research Institute, National Institute of Advanced Industrial Science and Technology, Japan
1-1-1 Umezono, Tsukuba, Ibaraki 305-8562, Japan

Introduction

Hydrogenated amorphous Si (a-Si:H) is a semiconductor material useful to 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 semiconducting films, here we propose a novel method of material synthesis; i.e. formation and deposition of transition metal (*M*) encapsulating Si clusters $M\mathrm{Si}_n$ (n= 8-16)[2].

The $M\mathrm{Si}_n$ 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 MoSi_{12}. Reflecting the large E_{HL}, clusters-assembled films of the $M\mathrm{Si}_n$ are expected to be semiconductor materials. In fact, the atomically thin layered film $(\mathrm{MoSi}_{12})_n$ 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 $M\mathrm{Si}_n$ (*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 $M\mathrm{Si}_n$ cluster assembled films

The $M\mathrm{Si}_n$ cluster films were synthesized by deposition of hydrogenated $M\mathrm{Si}_n$ ($M\mathrm{Si}_n\mathrm{H}_x$) clusters onto silica substrates at room temperature (RT) followed by annealing at ~500℃ for 10 minutes in an ultra high vacuum for dehydrogenation. The $M\mathrm{Si}_n\mathrm{H}_x$ clusters were synthesized by reaction between SiH_4 molecules and *M* atoms supplied by laser ablation. The laser pulses were focused onto *M* targets in a silane SiH_4 pressure of 3-20 Pa. We measured compositions of the $M\mathrm{Si}_n$ films using Rutherford back scattering and XPS. Compositions of the $M\mathrm{Si}_n$ films were controlled by the SiH_4 pressure. In the film, the $M\mathrm{Si}_n$ clusters were not crystallized but randomly connected with each other.

Results and Discussion

Figure 2 shows Raman scattering spectra of MoSi_{12} and NbSi_{13} 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 2*p* and Nb 3*d* from the NbSi_{13} 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 3*d* peaks. In other words, the Nb atoms were not oxidized by the air expose. This indicates that Nb atoms are encapsulated in Si networks in the NbSi_{13} cluster film. To identify local structure, we measured XAS for the WSi_n (n~10) films. Results of the XANES and EXAFS of the W L_3 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 WSi_{10} film actually consists of WSi_{10} clusters.

To investigate the electronic structure of $M\mathrm{Si}_n$ cluster films, we measured optical-absorption spectra. The optical gap E_{og} of ~1 eV was observed for WSi_{10} and MoSi_{12} cluster films by estimation using the Tauc plot as shown in Fig. 4. Figure 5 shows variation of E_{og} values depending on the n value. When the n value reaches 5, we found the rise of E_{og}, indicating that $M\mathrm{Si}_n$ ($n \geqq 5$) cluster films have a semiconducting energy gap. The E_{og} increases with increase of n and reaches ~1 eV for n~10 reflecting the large E_{HL} gap of the free $M\mathrm{Si}_n$ clusters.

As shown in Fig. 6, electrical resistivity ρ of the $M\mathrm{Si}_n$ 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 $M\mathrm{Si}_n$ (n~10) cluster films mentioned above. We measured temperature dependence of conductivity σ (= 1/ ρ) for MoSi_n (n= 5, 9, 12 and 16) cluster films (Fig. 7). The σ increased with decrease of the substrate temperature. This indicates that the MoSi_n cluster films have a semiconducting transport

property. Activation energies E_a of σ were calculated from the σ-1/T 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_{og} 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 property 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 MSi_n clusters as a building block of the films.

Conclusions

In conclusion, the MSi_n (M= Mo, Nb and W) cluster assembled films are synthesized by the deposition of MSi_nH_x clusters onto solid substrates followed by thermal annealing at ~500℃. 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 ~10, the MSi_n cluster film is a semiconductor with the gap of ~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 MSi_n cluster film will be an attractive material for thin film devices.

Acknowledgement

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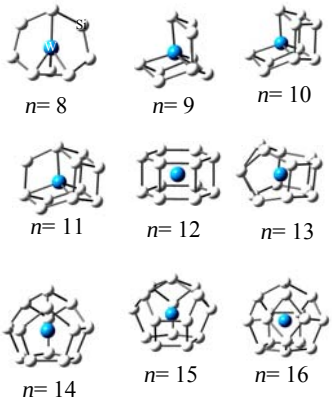

Figure 1: Optimized structures of WSi_n (n=8-16) clusters by *ab initio* calculations (Gaussian 03 B3PW91/LanL2DZ).

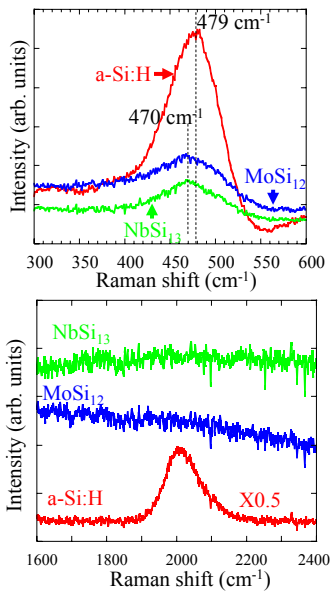

Figure 2: Microscopic Raman scattering spectra of $MoSi_{12}$, $NbSi_{13}$ cluster films and the a-Si:H film.

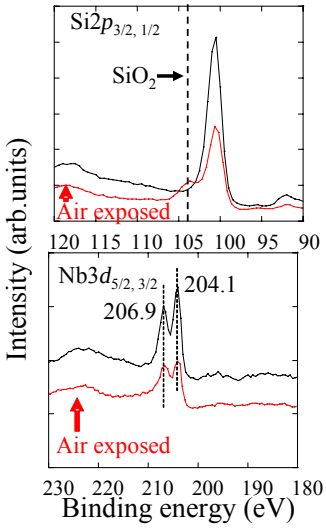

Figure 3: XPS spectra of Si 2p and Nb 3d from the $NbSi_{13}$ cluster film before and after the air exposure.

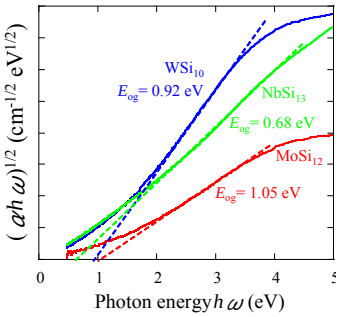

Figure 4: Tauc plots for WSi_{10}, $MoSi_{12}$ and $NbSi_{13}$ cluster films.

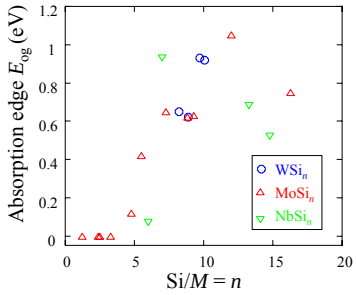

Figure 5: Variation of E_{og} depending on the n value of MSi_n cluster films.

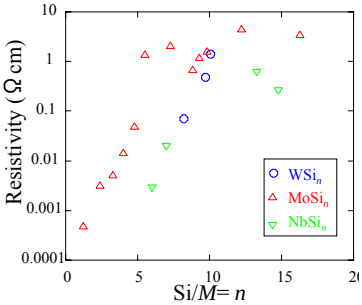

Figure 6: Resistivity of the MSi_n films at RT as a function of Si content n.

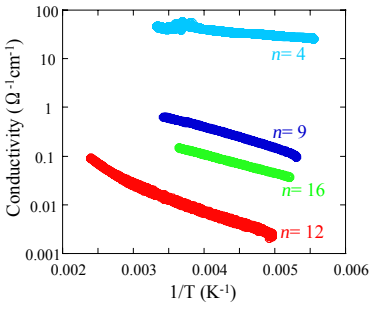

Figure 7: Temperature dependence of conductivity σ(= 1/ρ) for $MoSi_n$ (n= 5, 9, 12 and 16) cluster films.