Transactions of the Materials Research Society of Japan 25 [4] 1003-1006 (2000)

Electronic and geometric structures of metal-silicide clusters

M. Sanekata, T. Koya, S. Nagao, Y. Negishi, A. Nakajima, and K. Kaya*

Department of Chemistry, Faculty of Science and Technology, Keio University,

3-14-1 Hiyoshi, Kohoku-ku, Yokohama 223-8522, Japan

Fax: 81-45-563-5967, e-mail: nakajima@iw.chem.keio.ac.jp

*Institute for Molecular Science

Fax: 81-564-55-4386, e-mail: kaya@ims.ac.jp

Negative/positive ions of W-silicide cluster are produced by a laser vaporization source for two rods of W and Si. The W-silicide clusters with a metal atom, WSi_n, are only observed for the size-range of $n \geq 4$ in the mass spectrum and but are exclusively observed for $n \geq 6$. Especially, $WSi_{15}^{\pm}$ as well as WSi_{16}^{+} are remarkably stable comparing with $WSi_n^{\pm}$ of the neighboring sizes. Photoelectron spectra for their negative ions and the adsorption reactivities toward H_2O suggest that the stability of $WSi_n^{\pm}$ for $n \geq 10$ is due to the geometric structure containing a metal atom.

Key words: metal-silicide cluster, electronic structure, geometric structure, photoelectron, reactivity

1. INTRODUCTION

Metal silicides (MSi, MSi_2, and M_2Si etc.) are extensively used as a Schottky-barrier material at the metal-semiconductor connection in semiconductor devices[1, 2]. Meanwhile, semiconductor clusters and their quantum dots have been known to show size-dependent band gaps due to cluster size/quantum size effect[3]. Metal-silicide clusters are also expected to be as a *cluster material* which show the band gap and the electronic properties with these size dependences.

In this article, we investigate the photoelectron spectra and the adsorption reactivities of W-silicide clusters (WSi_n) using the photoelectron spectroscopy for negative ions and chemical probe method for positive ions. The size evolution toward the photoelectron spectra of WSi_n^- and the adsorption reactivity of WSi_n^+ suggests the existance of the bimodal geometric structures. We will discuss on the stability, connecting with the geometric properties.

2. EXPERIMENTAL

The experimental setup was described in detail previously[4, 5]. Briefly, the metal-silicide cluster negative/positive ions are produced by a laser vaporization source. The second harmonics of two Nd:YAG lasers (532 nm) were focused on to a W and a Si rods individually. As for photoelectron spectroscopy for negative ions, the formed negative ions were introduced via a skimmer into a time-of-flight (TOF) mass spectrometer. In the photodetachment region, the mass-selected negative ions were photo-detached by the fourth harmonics of a pulsed Nd:YAG laser (266 nm; 4.66 eV). The photoelectron spectra were recorded by measuring the kinetic energy of electrons photo-detached from the negative ion, using a magnetic-bottle type photoelectron spectrometer. While, the adsorption reactivity of WSi_n^+ with H_2O was examined employing the flow-tube reactor (FTR) combined with the double-rod laser vaporization source[5, 6]. The reactant H_2O seeded in helium gas at room temperature was injected into FTR, at which a pulsed valve was synchronized with the passing bunch of metal-silicide clusters. In order to estimate the reactivity, the mass spectra were recorded in the presence and absence of reactant.

3. RESULTS AND DISCUSSION

3.1 Mass Spectroscopy of WSi_n^-

Fig.1 shows TOF mass spectra of negative-ion species produced from a double-rod laser vaporization source toward the W and the Si rod. As shown in Fig.1, two major species were found in the mass spectrum. The species are as follows: silicon clusters (Si_n^-) in smaller mass range and W-silicide clusters ($W_mSi_n^-$) in larger one. The Si_n^- clusters have already been known to show the characteristic size distribution resulting from thermal fragmentation[7]. The present Si_n^- dis-

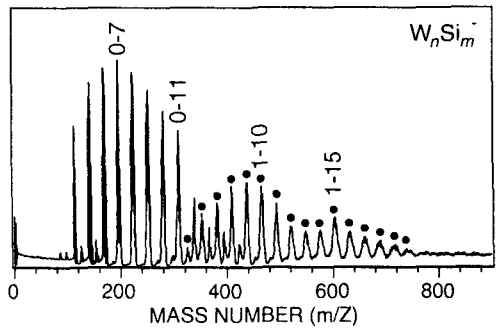

Figure 1: Typical TOF mass spectra of W-silicide cluster negative ions obtained from a double-rod laser vaporization source. The filled circles (•) represent the mass peak for major W-silicide clusters.

tribution observed in this mass spectrum is expected to reproduce the previously reported result. Meanwhile, for W-silicide clusters, WSi_n^- containing a W atom was only observed in the size range of $n \geq 4$ and existed dominantly in the size range around $n \sim 10$, but no W-silicide cluster containing multiple W atoms was observed throughout the present work. Moreover we unexpectedly found that WSi_{15}^- was a prominent species comparing with ones of the neighboring sizes. Similar trend has been observed for the positive ions: WSi_{15}^+ and WSi_{16}^+ are stable as quite magic numbers[9, 10]. Comparing WSi_n^- with Si_n^-, WSi_n^- clusters are expected to be stable with more Si atoms rather than pure Si_n^-. In order to reveal whether this trend is due to the electric properties or due to the geometric ones, we will discuss the photoelectron spectroscopy of WSi_n^- in next section.

3.2 Photoelectron Spectroscopy of WSi_n^-

Fig.2 shows the photoelectron spectra of metal-silicide cluster negative ions WSi_n^- (n = 4-17), using a 266-nm-ptotodetachment laser. The electron affinities estimated from the appearance thresholds of photoelectron ejection are as shown in Fig.2. The photoelectron spectra of Si_n^- clusters at 266 nm have been reported in the same size range[11, 12]. The silicon cluster negative ions were categorized into two characters in the neutral electronic structures; closed-shell clusters (n = 4, 6, 7, 10, and 11) with an isolated small bump in their photoelectron spectra, which enable us to estimate the HOMO-LUMO gap, and open-shell clusters (n = 3, 5, 8, and 12)

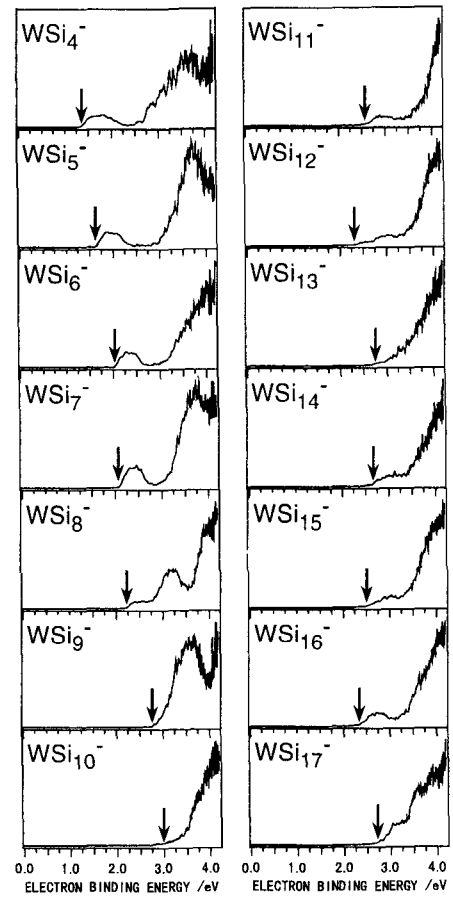

Figure 2: Photoelectron spectra of WSi_n^- (n = 4-17) obtained at 266 nm (4.66 eV). Arrows at the spectral threshold mark the electron affinities.

without the bump.

For WSi_n^-, the distinct bump is clearly found in the photoelectron spectra for the sizes of n = 4-8. Then the HOMO-LUMO gaps are expected once to converge into a single peak at n = 10. For $n \leq 9$, the spectral profiles of WSi_n^- and of Si_n^- are more alike except for small open-shell clusters of n = 3, 5, and suggestively 8. In the photoelectron spectra of these open-shell clusters, a new small bump appears. This behavior could be explained by one-electron transfer into a LUMO level of bare silicon cluster from metal atom. On the contrary, the small bump abruptly disappears from the photoelectron spectrum of WSi_{10}^- although the bump has been observed in the spectra of Si_n^-. The small-bump vanishing at n = 10 suggests that strong chemical bondings are formed among a W atom and Si atoms, and that WSi_{10}^- prefers to have some geometric structure with more rich interaction on W-Si.

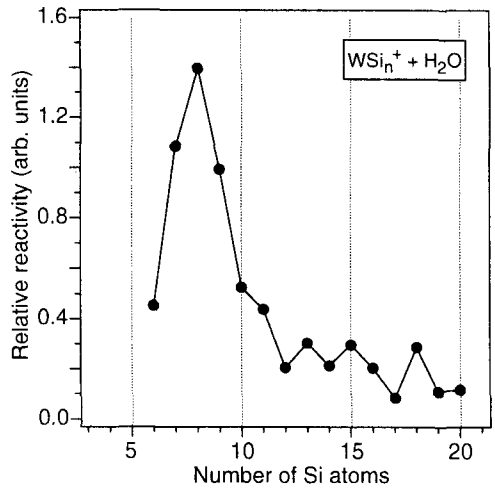

Figure 3: Relative adsorption reactivities of WSi_n^+ with H_2O.

Over $n = 11 - 15$, the bump at threshold is inconspicuous, and the spectral profiles are quite similar to that of $n = 10$. These points suggest that WSi_{10}^- for $n \geq 10$ have in common the similar core to WSi_{10}^-. In order to conjecture those geometric structures, we examine the adsorption reactivition of W-silicide clusters.

3.3 Adsorption reaction of WSi_n^+ with H_2O

The chemical probe method using FTR has the advantage of roughly estimating the geometric structure and the location where a reactive center is located in/on the cluster[6, 8]. The mass spectra were recorded in the presence/absence of reactant H_2O (~0.6 %) seeded in helium gas. As the mass peak of prepared clusters is I_0 and one of remaining clusters I, the reactivity R is described by $R = -\ln(I/I_0)$.

Fig.4 shows the reactivity of WSi_n^+ clusters with H_2O obtained from the chemical probe experiment. This size-dependent reactivity is roughly divided into two regions; (1) high reactivities for $7 \leq n \leq 9$ and (2) relatively smaller ones for $n \geq 10$. These trends are quite similar between WSi_n^- and WSi_n^+ independent of their charges[14]. The reacitivities of Si_n^+ with H_2O and D_2O provide us with a hint to understand the interaction of WSi_n^+ clusters with H_2O. According to previously reported results of Si_n^+, the reactivity for $n \leq 6$ decreases with n and one for $n = 5$ and 6 is negligibly small[13]. While, the reactivity for $n = 10 - 30$ strongly shows the size-dependence, and especially Si_{11}^+, Si_{13}^+, Si_{14}^+, Si_{19}^+, and Si_{23}^+ are unreactive[8]. Therefore, as shown in Fig.4, the behavior for reactivity of WSi_n^+ is quite different from that of Si_n^+. Consequently, this is suggested that the reactivity of $WSi_n^\pm$ is drastically affected by the W-H_2O interaction. Indeed, we observed the striking reaction of W^+ with H_2O in the mass spectrum; $W^+ + x(H_2O) \rightarrow WO_n^+$ ($n = 1 - 3$). Assuming that W atom behaves as a reaction center, the behaviors of the size-dependent reactivities for (1) and (2) as mentioned above are easily understandable. However, it is impossible to explain the abrupt depression at $n = 10$. For negative ions as shown in Fig.4, we observed quite similar behavior for the size-dependent reactivity, although the signal intensities were far lower in the chemical-probe experiment for negative ions than for positive ions. It is conjectured that the depression at $n \geq 10$ is due to geometric structure rather than due to the electronic structure, and that the geometric structure at $n \geq 10$ changes suddenly into the structure that the reaction-centered metal is besieged by silicon atoms. As mentioned previously, the photoelectron spectra of $n = 10$ feasibly indicate the structural change. For $n = 10$, the interstitial structure, which prefers the direct W-Si interaction, should be supported in this work as S. M. Beck said[9, 10]. In the same way as $n = 10$, another $WSi_n^\pm$ clusters for $n \geq 10$ consist of such metal-centered structure. The drastical change at $n = 10$, which the location of metal atom transfers from the surface to the inside of Si_n cluster, is expected to involve with as a microscopic phase transition in silicide crystals. For WSi_{15} behaving as a magic number, the cluster is stabilized from the geometric property rather than electronic ones because there is no serious difference among the photoelectron spectra of $n = 14 - 15$. At present, we also have no results on the structure of $WSi_{15}^\pm$ supported by theoretical calculation. However $WSi_{15}^\pm$ structure is expected to be close to the substitutional one consisting of WSi_{16} unit extracted from diamond structure of bulk Si crystal.

4. CONCLUSIONS

In this article, we have investigated the electronic and geometric structures of the W-silicide clusters, $WSi_n^\pm$, using the photoelectron spectroscopy and the chemical-probe method. Both of the photoelectron spectra for negative ions and the chemical reactivities with H_2O indicate that a W atom is located on the surface of Si

cluster for $n \leq 9$ and in the network of Si cluster for $n \geq 10$. In the latter clusters, the WSi_{15}^- is particularly stable as a magic cluster. This stability for $n = 15$ as well as $n \geq 10$ is attributed to arising from the geometric structure rather than the electronic one. These behaviors may be concerned in the microscopic feature toward the infiltration of metal impurity into silicon crystal.

ACKNOWREDGEMENTS

This work was supported by a program entitled "Research for the Future" of the Japan Society for the Promotion of Science (No. 98P01203) and by a Grant-in-Aid for Scientific Research (No. 12740326) from the Ministry of Education, Science and Culture of Japan.

REFERENCES

[1] S. M. Sze, Physics of Semiconductor Devices, Wiley, New York, 1981.

[2] W. Mönch, Surf. Sci. 299/300 (1994) 928.

[3] S. V. Gaponenko, Optical Properties of Semiconductor Nanocrystals, Cambridge Univ. Press, 1998.

[4] A. Nakajima, T. Taguwa, K. Hoshino, T. Sugioka, T. Naganuma, F. Ono, K. Watanabe, K. Nakao, Y. Konishi, R. Kishi, K. Kaya, Chem. Phys. Lett. 214 (1993) 22.

[5] S. Nagao, T. Kurikawa, K. Miyajima, A. Nakajima, K. Kaya, J. Phys. Chem. A 102 (1998) 4495.

[6] M. E. Guesic, M. D. Morse, S. C. O'Brien, R. E. Smalley, Rev. Sci. Instrum. 56 (1985) 2123.

[7] L. A. Bloomfield, M. E. Geusic, R. R. Freeman, W. L. Brown, Chem. Phys. Lett. 121 (1985) 33.

[8] U. Ray, M. F. Jarrold, J. Chem. Phys. 94 (1991) 2631.

[9] S. M. Beck, J. Chem. Phys. 90 (1989) 6306.

[10] S. M. Beck, Advances in Metal and Semiconductor Clusters, 1 (1993) 241.

[11] O. Cheshnovsky, S. H. Yang, C. L. Pettiette, M. J. Craycraft, Y. Liu, R. E. Smalley, Chem. Phys. Lett. 138 (1987) 119.

[12] H. Kawamata, Y. Negishi, R. Kishi, S. Iwata, A. Nakajima, K. Kaya, J. Chem. Phys. 105 (1996) 5369.

[13] W. R. Creasy, A. O'Keefe, J. R. McDonald, J. Phys. Chem. 91 (1987) 2848.

[14] M. Sanekata, S. Nagao, Y. Negishi, T. Koya, A. Nakajima, K. Kaya, *to be submitted*

(Received December 17, 1999; Accepted August 31, 2000)