Eur. Phys. J. D **16**, 271–274 (2001)

THE EUROPEAN
PHYSICAL JOURNAL D
EDP Sciences

Electronic properties of assembled islands of hydrogen-saturated silicon clusters on Si(111)-(7x7) surfaces studied by scanning tunneling spectroscopy

L. Bolotov[1,a], N. Uchida[2], and T. Kanayama[2,b]

[1] Joint Research Center for Atom Technology (JRCAT), Angstrom Technology Partnership, 1-1-1 Higashi, Tsukuba, Ibaraki 305-0046, Japan
[2] JRCAT, National Institute of Advanced Industrial Science and Technology (AIST), 1-1-1 Higashi, Tsukuba, Ibaraki 305-8562, Japan

Received 30 November 2000

Abstract. We present results of scanning tunneling spectroscopy (STS) measurements of hydrogen-saturated silicon clusters islands formed on Si(111)-(7×7) surfaces. Nanometer-size islands of Si_6H_{12} with a height of 0.2-4 nm were assembled with a scanning tunneling microscope (STM) using a tip-to-sample voltage larger than 3 V. STS spectra of Si_6H_{12} cluster islands show characteristic peaks originating in resonance tunneling through discrete states of the clusters. The peak positions change little with island height, while the peak width shows a tendency of narrowing for the tall islands. The peak narrowing is interpreted as increase of lifetime of electron trapped at the cluster states. The lifetime was as short as 10^{-13} s resulting from interaction with the dangling bonds of surface atoms, which prevents charge accumulation at the cluster islands.

PACS. 61.16.Ch Scanning probe microscopy: scanning tunneling, atomic force, scanning optical, magnetic force, etc. – 61.46.+w Nanoscale materials clusters, nanoparticles, nanotubes and nanocrystals – 36.40.Cg Electronic and magnetic properties of clusters – 73.50.-h Electronic transport phenomena in thin films

1 Introduction

Charge transport in nanostructures is of fundamental importance in physics and electronics. In particular, transport of electrons in individual molecular structures and nanocrystals is affected by quantum phenomena such as size quantization and Coulomb blockade yielding new operation principles of nanometer-scale devices. For example, it has been demonstrated that a layer of conjugated organic molecules placed between two metal electrodes has diode-like electronic characteristics originating in the spatial asymmetry of the molecule structure [1,2]. In the same way, gold nanocrystals of 5.8 nm diameter linked to metal leads have shown oscillations in tunneling conductance originating in Coulomb interaction of transit electrons with a charge trapped in the nanocrystal [3,4]. These results, on one hand, have stimulated activities to fabricate electronic devices using molecules as active components [5–7]. On the other hand, electron transport through individual nanostructures has extensively been studied from theoretical point of view, demonstrating its sensitivity to coupling between the molecule and the substrate [8,9].

Recently, significant interest has been addressing to small semiconductor clusters since their physical properties are widely tunable with size, structure and composition. A cluster growth technique [10,11] providing composition control and size selection of clusters allows us to study hydrogenated silicon clusters Si_nH_x ($n = 3$–8) assembled on solid surfaces. We have already reported that hydrogen-saturated silicon cluster cations $Si_6H_{13}^+$ were generated in an ion trap and deposited on Si substrates [12]. The $Si_6H_{13}^+$ cations were converted on the surface to the neutral Si_6H_{12} structure and were partially ordered at surface steps and domain boundaries [12,13]. Scanning tunneling spectroscopy (STS) of an isolated cluster showed characteristic peaks corresponding to resonance tunneling in discrete states of the cluster broadened by interaction with the dangling-bonds of surface atoms [13].

In this paper we present scanning tunneling spectroscopy study of Si_6H_{12} islands prepared on Si(111)-(7×7) surfaces. These islands were precisely formed with a scanning tunneling microscope (STM). Tunneling spectroscopy of the prepared islands shows variation in electron transport through cluster nanostructures with their height when the height is smaller than ~ 1 nm.

---

[a] e-mail: `bolotov@jrcat.or.jp`
[b] e-mail: `kanayama@jrcat.or.jp`

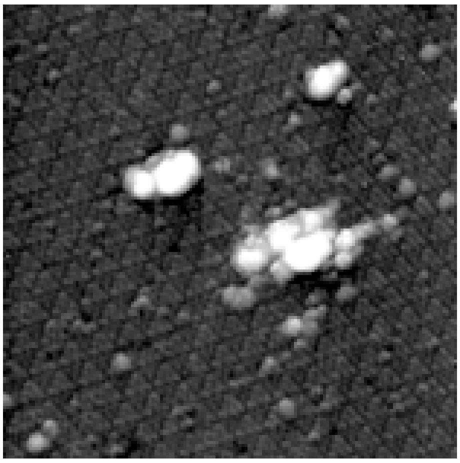

Fig. 1. An STM image (80×80 nm^2, -1.7 V, 0.12 nA) of three assembled islands consisting of Si_6H_{12} clusters on the Si(111)-(7×7) surface. The assembling was performed while keeping the bias voltage at -3 V with the tunneling current of 0.12 nA. For duration of $\sim$ 4 s, $\sim$ 6 s and $\sim$ 12 s the islands were grown to the apparent height of 0.21 (at the top), 0.34 (on the left-hand side) and 0.52 nm (at the bottom) corresponding to apparently 1, 2 and 3 cluster layers, respectively.

2 Experiment

The Si_6H_{12} clusters were synthesized using the cluster-ion growth technique and the deposition equipment described previously [10,12]. Hydrogen-saturated Si cluster cations $Si_6H_{13}^+$ were grown from silane (SiH_4) gas with H_2 ambient gas in an ion trap through reaction between SiH_x^+ ions and radicals. Thus prepared cluster cations were mass-selectively ejected as an ion beam with kinetic energy of 18 ± 1 eV. The beam energy was reduced to 6 and 12 eV by applying retarding voltages to the substrate in order to achieved non-destructive deposition of the clusters. Clean Si(111)-(7×7) surfaces prepared from Si(111) wafers (n-type, 0.001 Ω cm, arsenic doped) were exposed to the cluster-ion beam at room temperature (RT). The cluster density of 2×10^{11}-2×10^{12} cm^{-2} was achieved for the cluster beam current of 4-20 pA. The cluster assembling and characterizations were performed at residual pressure of $\sim 5 \times 10^{-9}$ Pa with an STM operating at RT in the constant current mode with tunnel currents of 0.1-0.5 nA. We used W(111) tips having the radii less than 10 nm which were treated *in situ* with field-ion microscopy.

3 Island formation

Nanometer-scale islands of the deposited clusters were prepared by assembling the clusters with STM tips using the tip-to-sample bias voltage exceeding 3 V. At the bias voltage below 3 V the deposited clusters remained stationary [13]. When observed with low voltages, the clusters appeared as bright circular protrusions and were randomly distributed along the surface, statistically, preferring to stay in faulted halves of the (7×7) unit cell. Beyond the threshold of 3 V the cluster became mobile and accumulated at the tip position. Fig. 1 shows an STM image of three assembled islands consisting of Si_6H_{12} clusters on the Si(111)-(7×7) surface. The small island (in the upper-center) were formed in $\sim$ 4 s to a size of $\sim$ 5 nm diameter and 0.21 nm height. The largest one was grown in $\sim$ 12 s to a height of $\sim$ 0.52 nm. The cluster islands were composed of individual clusters separated by $\sim$ 1 nm distance as shown in Fig. 2.

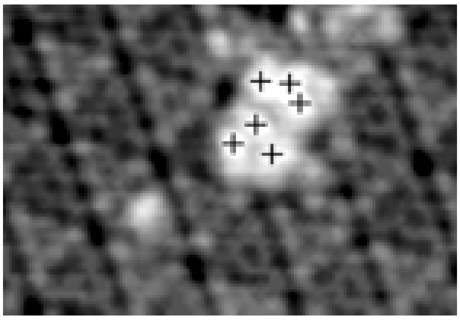

Fig. 2. A high-resolution STM image (16×11 nm^2, -1.5 V, 0.2 nA) of an island consisting of six Si_6H_{12} clusters. The island was prepared at the sample bias of -3 V on the surface with the cluster density of $\sim 10^{12}$ cm^{-2}. The crosses indicate the cluster positions. The clusters are separated by $\sim$ 1 nm distance.

The islands were prepared at both polarities of the bias voltage. The threshold voltages for cluster assembling were about -3 V and $+3$ V. The lack in polarity dependence suggests that the clusters are neutral on the surface in contrast to the situation that charged Cs atoms on GaAs(110) surfaces were agglomerated with STM only at positive sample bias [14]. The fact that individual clusters in the small islands are resolved (see Fig. 2) with separation as close as 1 nm also indicates the agglomeration of neutral clusters. Agglomeration of neutral clusters agrees with neutralization of the cluster ions on the surface by losing one hydrogen atom reported previously [13].

The islands with a height of 0.2-4 nm were prepared consisting of apparently 1 to $\sim$ 10 cluster layers since the calculated height of the Si_6H_{12} is 0.384 nm [15]. The true height of the islands is difficult to determine from topographical data since the tip movement represents distribution of electron density at the surface and is sensitive to the electron states of the cluster. In order to get comparable STS data we measured the height of the cluster islands from the dangling bonds of the adatoms at -1.7 V and the tunneling resistance of 8-12 GΩ.

4 Tunneling spectroscopy

Figure 3 shows the STS spectra observed over prepared islands. Spectroscopy data were acquired while keeping the tip position fixed directly over the top of the islands. In order to avoid the cluster displacement at the large bias voltage, the *I*-*V* spectra were measured within the range of $-2 \cdots + 2$ V at the tunneling resistance of 8-12 GΩ. The conductance spectrum (I/V) for each island

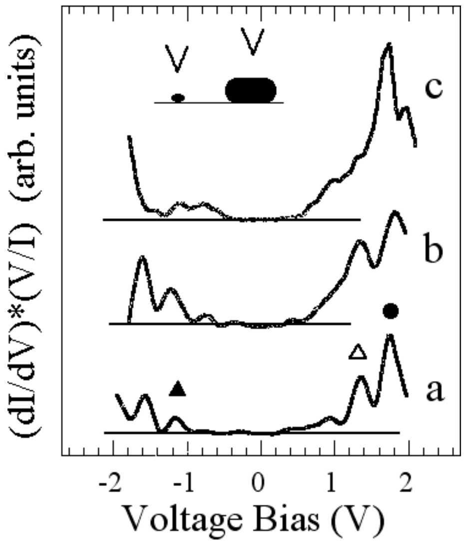

Fig. 3. STS spectra over assembled islands with a height of 0.21 (a), 0.52 (b) and ~ 4 nm (c). The characteristic peaks at about +1.8 V (filled circules), +1.3 V (open triangles) and −1.2 V (filled triangles) are indicated. The tunneling resictance was 12 GΩ.

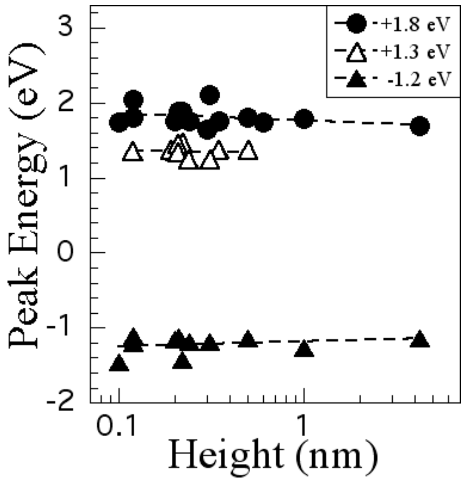

Fig. 4. Energy of characteristic peaks observed in STS spectra at about +1.8 V (filled circules), +1.3 V (open triangles) and −1.2 V (filled triangles) plotted as a function of Si_6H_{12} island height. The peak energy was determined by fitting STS spectra with Lorentzian functions. The dashed lines are eyeguides.

was fitted to an exponential function, and the differential conductance (dI/dV) was normalized by the (I/V) fitted function. As is conventional to semiconductor surfaces, the $(dI/dV)/(I/V)$ spectrum reflects density of states for single electron tunneling, identifying electronic structure of an adsorbate. We see peaks in the STS spectra at about +1.8 V, +1.3 V (empty states) and about −1.2 V (filled states). These peaks were observed in every STS spectrum of the prepared islands, suggesting to be characteristic for the cluster nanostructures.

In order to determine the peak position E_0 and the peak width Γ, we fitted the peak by a Lorentzian function $(A_0/[(E-E_0)^2+\Gamma^2])$, where A_0 is a constant, as was employed in resonance tunneling spectroscopy of atoms adsorbed on metal surfaces [16]. Fig. 4 shows the peak energy plotted as a function of the island height. The characteristic peaks shifted little with the island height. As the similar peaks in STS spectra were observed over the isolated Si_6H_{12} clusters, this observation indicates that the assembled clusters preserved their original electronic states even when assembled.

Fig. 5 shows change of the peak widths as a function of island height. For small islands the peak width varies from 0.2 to ~ 1.2 eV. The peak width observed is larger than the thermal broadening of ~ 5.4 kT (~ 140 meV) and, thus corresponds to lifetime broadening of the cluster state [4,16]. The lifetime of electrons at the cluster state is given by $\tau = h/\Gamma$, where h is the Plank constant. For small islands the lifetime is on the order of 10^{-13}-10^{-14} s.

The effect of lifetime broadening on atomic levels is well known for resonance tunneling of field-emitted electrons through adsorbates in proximity to a metal surface. For example, the atomic levels of Zr and Ba atoms adsorbed on the W(111) surface was broadened to ~ 1 eV resulting from interaction with the continuum of metal states [17,18]. In the case of the Si_6H_{12} clusters adsorbed on the Si(111)-(7×7) surface, the lifetime broadening occurs owing to interaction with underlying dangling bonds of the surface atoms. Considering different adsorption sites of the clusters in the (7×7) unit cell [13], the cluster-surface interaction is position-dependent, thus leading to change of the electron lifetime with the adsorption site.

For multi-layer islands the peaks become narrower as seen in Fig. 5. The peak narrowing with island height is interpreted as increase in electron lifetime. The interaction with the surface dangling bonds decreases with the distance from the surface and becomes less effective above ~ 0.6 nm (see Fig. 5), thus increasing the electron lifetime in a cluster state. Dependence of excited molecule lifetimes on distance from a conductive surface has been reported in the literature [19,20]. For example, for C_{60} molecules separated from the gold substrate by alkanethiol layers, the lifetime showed the cube dependence on the separation distance, and was ~ 4.2×10^{-11} s for ~ 1.2 nm distance [20]. For pyrene molecules separeted from the Si(111) surface by Xe spacer layers of ~ 1.7 nm thick, it was ~ 3×10^{-9} s [19]. In the present case, the cluster-surface distance is as small as 0.2-0.6 nm resulting in the shorter lifetime (~ 10^{-13} s). In our experiments determination of the electron lifetime was done only for small islands when the peak width was larger than the thermal broadening limit (~ 140 meV). Even for the islands of ~ 0.6 nm thick, the electron lifetime is three orders of magnitude shorter than the tunneling time of ~ 10^{-10} s, which prevents charge accumulation at the cluster islands. Consequently, the Coulomb blockade effect is evidently restricted. This conclusion was confirmed by insensitivity of the peak energies to the tunneling resistance in the range

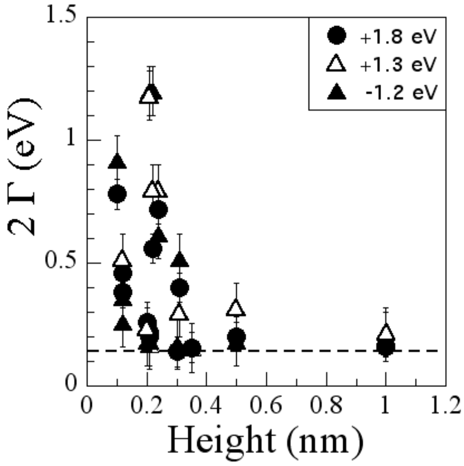

Fig. 5. Peak width (2Γ) corresponding to characteristic peaks in STS spectra at about +1.8 V (filled circules), +1.3 V (open triangles) and −1.2 V (filled triangles) plotted as a function of Si_6H_{12} island height. The peak width was determined by fitting STS spectra with Lorentzian functions. The dashed line indicates the thermal broadening limit at 300 K. The width is large for the Si_6H_{12} islands smaller than 0.6 nm.

of 1-12 GΩ, contrasting to the dependence of the Coulomb blockade effect on the tunneling resistance.

5 Conclusion

Nanometer-size islands of hydrogen-saturated silicon clusters Si_6H_{12} with a height of 0.2-4 nm were assembled with an STM using the bias voltage above 3 V. The formation of cluster islands allows us to elucidate electron transport in cluster nanostructures as a function of their size. STS spectra of the islands showed characteristic peaks originating in resonance tunneling through discrete states of the Si_6H_{12} cluster. The lifetime of electron at the cluster state increases with the island height and is as short as 10^{-13} s due to a proximity to the surface dangling bonds, which prevents charge accumulation at the cluster islands.

Authors thank Dr. T. Miyazaki (AIST) for theoretical calculations of cluster structures and invaluable discussions. This work was supported in part by New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

1. A.S. Martin, J.R. Sambles, G.J. Ashwell, Phys. Rev. Lett. **70**, 218 (1993).
2. M.A. Reed, C. Zhou, C.J. Muller, T.P. Burgin, J.M. Tour, Science **278**, 252 (1997).
3. D.L. Klein, P.L. McEuen, J.E.B. Katari, R. Roth, A.P. Alivisatos, Appl. Phys. Lett. **68**, 2574 (1996).
4. O. Millo, D. Katz, Y.W. Cao, U. Banin, Phys. Rev. B **61**, 16773 (2000).
5. J. Chen, M.A. Reed, A.M. Rawlett, J.M. Tour, Science **286**, 1550 (1999).
6. A. Dhirani, P.-H. Lin, P. Guyot-Sionnest, R.W. Zehner, L.R. Sita, J. Chem. Phys. **106**, 5249 (1997).
7. C. Joachim, J.K. Gimzewski, Chem. Phys. Lett. **265**, 353 (1996).
8. W. Tian, S. Datta, S. Hong, R. Reifenberg, J.I. Henderson, C.P. Kubiak, J. Chem. Phys. **109**, 2874 (1998).
9. M. Di Ventra, S.T. Pantelides, N.D. Lang, Phys. Rev. Lett. **84**, 979 (2000).
10. T. Kanayama, Jpn J. Appl. Phys. **33**, 1792 (1994).
11. H. Hiura, T. Kanayama, Chem. Phys. Lett. **328**, 409 (2000).
12. M.O. Watanabe, T. Miyazaki, T. Kanayama, Phys. Rev. Lett. **81**, 5362 (1998).
13. L. Bolotov, N. Uchida, T. Kanayama, Surf. Sci. **462**, 85 (2000).
14. L.J. Whitman, J.A. Stroscio, R. A. Dragoset, R.J. Celotta, Science **251**, 1206 (1991).
15. T. Miyazaki, T. Uda, I. Stich, K. Terakura, Chem. Phys. Lett. **284**, 12 (1998).
16. S. Hansma, *Tunneling Spectroscopy* (Plenum Press, NY, 1982).
17. J.W. Gadzuk, Phys. Rev. B **1**, 2110 (1970).
18. E.W. Plummer, R.D. Young, Phys. Rev. B **1**, 2088 (1970).
19. A.P. Alivisatos, M.F. Arndt, S. Efrima, D.H. Waldeck, C.B. Harris, J. Chem. Phys. **86**, 6540 (1987).
20. K. Kuhnke, R. Becker, M. Eppe, K. Kern, Phys. Rev. Lett. **79**, 3246 (1997).