We studied geometric and electronic structures of a platinum cluster disk consisting 30 Pt atoms on the Si(111)-7 × 7 surface by STM experiments (see left panel) and first principles calculations. It was found that the high stability of the cluster disk on the Si surface originates from the platinum–silicide bonds as strong as ~45 eV per cluster, which are formed by electron transfer from the 5d orbital of the Pt atoms to the 3s and 3p ones of the Si atoms. This finding gives an essential interpretation to the experimental discovery that valence electrons in an occupied molecular orbital of the Pt30/Si system are distributed in a wider region than the locations of the Pt atoms. It appeared that electron accumulation at the interface between the cluster and the substrate induces two-dimensional charge polarization in a nanospace as shown in right panel due to a combination of a metallic nature of the cluster disk and a highly resistive nature of the Si surface.

1 Introduction

An atomic-scale electric field brings specific chemical and physical phenomena. For instance, when a molecule is put in the electric field, its chemical reactivity can be enhanced by strong Coulomb forces acting on electrons, holes and ions of the molecule; positively charged and negatively charged atomic groups in the molecule accept and donate electrons, respectively, to be reduced and oxidized. Another example is surface-enhanced Raman scattering (SERS), which is driven by local surface plasmon induced in the polarized molecule [1] or formation of a charge-transfer complex [2]. Atomic manipulation by means of scanning tunnelling microscopy (STM) utilizes the strong electric field applied between an STM probe and an object atom [3]. Field emission of electrons and ions from a sharp needle such as field emission microscope (FEM) and field ion microscope (FIM) is also due to an atomic-scale electric field applied at the needle end [4].

An interface between a supported nanoparticle and a substrate surface is one of the most promising spaces for the strong electric field with a single polarity (uni-polar electric field, hereafter). When a nanoparticle encounters a substrate surface, electrons are transferred between them as far as
equilibration of their chemical potentials in analogy of the contact potential. As a result, charge polarization and a strong electric field are induced at the nanointerface between them. An atomic cluster having a diameter of ~1 nm can provide such a charge-polarized nanointerface as small as a typical molecule, so that a uni-polar electric field is applied to a whole molecule adsorbed on the cluster–substrate interface.

As the region of the uni-polar electric field is mainly determined by a diameter of the cluster, quantitative investigation of the nanointerface requires a specimen consisting of uni-sized clusters constructed on a solid surface; hereafter, the size is defined as a number of atoms included in a cluster. A combination of a metal cluster on a semiconductor surface is one of the most preferable systems for the creation of the strong electric field, because extra charge in the cluster is delocalized in it due to its metallic character [5], while the counter charge is accumulated at the interface between the cluster and the substrate surface due to the covalent resistive character of the semiconductor. On these stand points, it has been found in the STM studies that charges are polarized two-dimensionally in a uni-sized monatomic-layered platinum cluster disk, Pt$_{N_1}$, constructed on a silicon surface [6–8]; the centre and the periphery of the cluster are charged positively and negatively, respectively [6]. Furthermore, the Pt$_{N_1}$ disk with $N > 20$ has a close-packed atomic configuration [6, 7], so that the positive charge is delocalized within the cluster disk [8]. Lin et al. [9] have reported that monatomic-layered gold clusters prepared on a thin MgO film on the Ag(001) surface exhibit two-dimensional quantum-well states due to accumulation of free electrons in a cluster by electron transfer from the Ag surface through the thin film. A theoretical study has also predicted that the negative charge is accumulated at the two-dimensional interface between a planar gold cluster (size of 20) and the MgO(100) thin film prepared on the Mo(100) surface, where the negative charge is due to electron transfer from the Mo surface to the cluster through the MgO layer [10]. This specific electronic structure leads to its specific catalytic activity [11]. Another aspect of the charge polarization has been reported by Bollinger et al. [12] that metallic edge states are localized at a periphery of a monatomic-layered MoS$_2$ cluster having a diameter of ~5 nm prepared on the reconstructed Au(111) surface [13]. Similar edge states have also been found in uni-sized one-dimensional atomic chains on solid surfaces [13–18]. Lagoute et al. [19] have shown electron confinement in uni-sized monatomic-layered copper clusters assembled by atomic manipulation on the Cu(111) surface.

In this relation, we employed first principles calculations along with STM observation for understanding relation between geometric and electronic structures of the Pt cluster disk constructed on the Si surface. In this report, we describe essence of the strong attractive interaction between the Pt$_{30}$ disk and the Si surface from the viewpoint of the electronic structure, and the charge polarization is interpreted by electron transfer from the Pt to Si atoms.

2 Experimental method We describe briefly the experimental procedure, as the details have been reported elsewhere [6–8]. The uni-sized monatomic-layered Pt$_{30}$ disks were prepared by impact [20] of uni-sized Pt$_{30}^+$ on the Si(111)-7 × 7 surface at a collision energy of 1.3 ± 0.2 eV per Pt atom at an ambient pressure of 6 × 10$^{-8}$ Pa [7], where Pt$_{30}^+$ were mass-filtered out of an intense Pt$_{30}^+$ beam extracted from a cluster ion source equipped with a magnetron sputtering device [7]. This procedure makes the Pt$_{30}$ disks stick firmly on the surface with a sticking probability of almost unity [7]. This specimen is transported to the STM device at a pressure less than 3 × 10$^{-8}$ Pa. The STM images and the space-resolved tunnelling spectra [6, 8] of the Pt$_{30}$ disks were measured at the sample temperature of 77 K and at an ambient pressure less than 5 × 10$^{-9}$ Pa. All the STM images were obtained with an identical STM probe in the constant tunnelling-current mode. The Si(111)-7 × 7 surface of 3 × 10 mm$^2$ was prepared from a wafer of arsenic-doped silicon having the (111) surface (ShinEtsu, 0.525-mm thick, a specific resistance of 0.01–0.02 Ω cm) by 20 sets of flashing and annealing at an ambient pressure less than 5 × 10$^{-8}$ Pa. The Si sample was always replaced before every irradiation of the cluster ions. The STM probe was prepared by electrochemical etching of a polycrystalline tungsten rod, followed by electron-bombardment heating at an ambient pressure less than 1 × 10$^{-7}$ Pa.

3 Computational method First principles density functional calculations [21] were employed to calculate the geometric and electronic structures of Pt$_{30}$ on the Si(111)-7 × 7 surface. The Si surface was modelled with a slab consisting of six Si atomic layers according to the DAS model [22], and its bottom was terminated with H atoms. The periodic boundary was constructed with a vacuum space of ~1 nm along the z-axis, and this space was ensured to separate the interaction between the system and their periodical images. A hexagonal planar Pt$_{30}$, which was obtained by fragmenting the monatomic-layered Pt(111) surface slab, was placed above the centre of two different sites, viz. the unfaulted half (UFH) and the faulted half (FH) of the Si(111)-7 × 7 surface. The geometry was optimized by the steepest descent approach, without consideration of any symmetry; we optimized the top three layers with a convergence criterion of the force of ions at 100 meV nm$^{-1}$, while the bottom three layers and hydrogen one were kept frozen. The atoms were described in the plane-wave-based projector augmented wave (PAW) formalism [23] and the exchange correlation energy was corrected by the generalized gradient approximation (GGA) [24]. The Brillouin zone of the periodic system was sampled at the Γ point. To obtain the density of states, non-self-consistence calculations are employed with sampling of 4 × 4 × 1 k-points.

4 Results

4.1 Experimental results Figure 1 shows an STM image of a Pt$_{30}$ disk fixed on the silicon surface and a trace of the STM probe during this STM observation along the
broken line shown in panel a. The apparent height of this cluster disk is 0.29 nm as shown in panel b, where it is measured from the mid-level between the adatom and the stacking fault layer of the Si(111)-7//2 surface [7]. The cluster height is approximated very well by the apparent one, because the probe–object distance remains almost constant during the probe scanning in the constant-current mode even over different atoms; this is due to significant change in the tunnelling current with the distance between the STM probe and the object [3]. Statistical analysis of the height measured for 36 different Pt30 cluster disks gives the average height of 0.233 nm with one standard deviation of 0.035 nm.

The deposition site of the cluster disk was also derived from the STM image, where it is defined hereafter as the centre of gravity of the cluster disk; for example the cluster disk shown in Fig. 1 should be located above the mid-point of the two-centre adatoms in the FH of the Si(111)-7//2 surface if the 7//2 reconstructed structure was maintained even after the cluster deposition. There appears no correlation between the height and the deposition site. Furthermore, no preferential deposition site is observed.

Figure 1 (a) STM image of a uni-sized platinum cluster disk, Pt30, deposited on the FH of the Si(111) surface and (b) trace of the STM probe along the broken line indicated in panel a. The STM image was measured at a temperature of 77 K at a constant tunnelling current of 1.0 nA by applying the bias voltage of −3.0 V applied to the surface sample, and hence this image and the trace (panel b) show the topographic profile of the cluster.

Figure 2 Correlation between the apparent height and the deposition site obtained from STM images measured for 36 Pt30 cluster disks deposited on the Si(111) surface. The marks denote the deposition sites with the height of 0.26 (●), 0.27 (○), 0.28 (□), 0.29 (∆), 0.30 (◇), 0.31 (○), 0.32 (●), 0.33 (○), 0.34 (□), 0.35 (◇) and 0.36 nm (▼).

Figure 3 shows a tunnelling spectrum measured by locating the STM probe above the centre of the Pt30 disk shown in panel a of Fig. 1, where the distance between the STM probe and the cluster disk was determined by the initial tunnelling current of 1.0 nA at the bias voltage, $V_s$, of −3.0 V applied to the surface sample. The uncertainty indicated as bars in Fig. 3 mainly originates from that in the tunnelling current, $I$. Peaks were reproducibly observed at $V_s = −1.5, −1.0, −0.5, 0.4, 0.9$ and $2.0$ V; those observed at the negative and positive $V_s$ are assigned to the occupied and unoccupied electronic levels of the cluster disk, respectively, and $V_s = 0$ corresponds to the chemical potential of the cluster–surface system. As the normalized differential conductance, $dI/dV_s/(I/V_s)$, is approximately proportional to the local density of electronic states, one can obtain the spatial distribution of the electrons in a given level by plotting $dI/dV_s/(I/V_s)$ at the corresponding $V_s$ as a function of the STM-probe position. It

Figure 3 Space-resolved tunnelling spectrum measured over a Pt30 cluster disk deposited on the FH of the Si(111) surface shown in Fig. 1, where the STM probe was located above the centre of this cluster disk; $I$ and $V_s$ are the tunnelling current and the bias voltage applied to the sample with respect to the STM probe. The spectrum was measured at a temperature of 77 K.
was found that the electrons in the occupied level at 1.5 eV below the chemical potential are distributed in a diameter of \( \frac{2}{\sqrt{C_0}} \) 0.2 nm (FWHM), which is meaningfully wider than the geometric diameter of this cluster disk (1.7 nm) [6].

4.2 Computational results

Figure 4 shows the optimized geometry of Pt30 deposited on the UFH of the Si surface. The cluster geometry and the top layers of the substrate are significantly distorted from the initial one as a result of increasing the Pt–Si bond strength. It was found that the strength of the Pt–Si bond is larger than that of the other ones. The calculated bond energy of the Pt–Si, Pt–Pt and Si–Si are 3.05, 1.98 and 1.84 eV, respectively, and the Pt–Si bond distance was calculated to be 0.228 nm. The adsorption energy, \( E_{\text{ad}} \), of this cluster is 44.54 eV (=1.485 eV per atom), which was calculated according to

\[
E_{\text{ad}} = E_{\text{Si}} + E_{\text{Pt}} - E_{\text{Pt@Si}},
\]

where \( E_{\text{Si}}, E_{\text{Pt}} \) and \( E_{\text{Pt@Si}} \) are total energies of the clean Si(111)-7 × 7 surface, the isolated and the supported Pt30, respectively. Similarly, the adsorption energy of the cluster deposited on the FH is 46.05 eV (=1.535 eV per atom).

Figure 5 displays partial densities of electronic states (PDOS) of Pt30 calculated by first principles calculations, where the cluster is deposited on the centre of the FH of the Si(111)-7 × 7 surface. The energy is measured with respect to the Fermi energy, \( E_F \).

\[\delta \rho = \rho(\text{Pt@Si}) - \rho(\text{Pt}) - \rho(\text{Si}),\]

where \( \rho(\text{Pt}) \), \( \rho(\text{Si}) \) and \( \rho(\text{Pt@Si}) \) are the total charge densities of the Pt30 cluster, the Si surface and the combined system, respectively. Figure 6 shows the charge density differences of the Pt30 disk deposited on the FH of the Si(111)-7 × 7 surface to understand the charge transfer mechanism in the system. The excess electrons are distributed in between the Pt30 disk and the Si surface, while the top of the Pt30 disk depletes electrons. The same kind of electron transfer was discernible in the calculations for the Pt30 disk on the UHF.

5 Discussion

5.1 Geometry of clusters

The first principles calculations reproduced the observed geometry of the monatomic-layered atomic configuration for the Pt30 placed
5.3 Electronic structure Our calculations revealed that the nature of the Pt–Si bonding is given by the electron transfer from the Pt-5d atomic orbital to the Si-3s and Si-3p ones. This electron transfer induces the two-dimensional charge polarization of the cluster disk as observed by the space-resolved tunnelling spectroscopy [6]; the valence electrons of the Pt$_{30}$ cluster disk in the occupied level at $-1.5$ eV are distributed out of the cluster disk, so that the centre and the periphery of the cluster disk are charged positively and negatively, respectively. Indeed, the calculations showed that the electron density is high in between the Pt atoms in the periphery of the cluster disk and the adjacent Si atoms as shown in Fig. 6. A similar phenomenon of the strong hybridization of the atomic orbitals has been observed in thin layers of platinum silicide; the Pt-5d orbitals are strongly mixed with the Si ones [26].

The negative charge is localized at the interface between the Pt cluster disk and the adjacent Si atoms due to the covalent bonding of the silicon atoms arranged in the amorphous structure around the cluster disk. On the other hand, the centre top of the cluster disk is charged positively. This is due to metallic nature of the cluster disk originating from the close-packed arrangement of the platinum atoms, that is delocalization of the positive charge all over the cluster disk by the delocalization of its rest of the 5d valence electrons to compensate high Coulomb energy.

6 Conclusions We conclude from the combination studies of the STM observation and the first principles calculations that the monatomic-layered geometry of the Pt$_{30}$ cluster disk on the Si(111) surface originates from strong bonding between the Pt and Si atoms by electron transfer from the Pt atoms to the adjacent Si atoms. Furthermore, this electron transfer induces the two-dimensional charge polarization with negative-charge accumulation at the interface between the cluster disk and the Si surface and positive-charge delocalization in the cluster disk. As a result, one can obtain strong electric field in a nanospace at the interface between the cluster disk and the Si surface.

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