

Nanospace charge polarization of monatomic-layered platinum cluster disk constructed on silicon(111)- 7×7 surface

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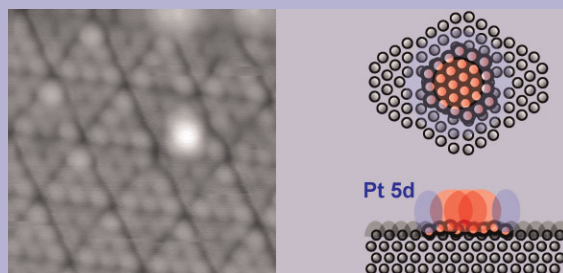
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We studied geometric and electronic structures of a platinum cluster disk consisting 30 Pt atoms on the Si(111)- 7×7 surface by STM experiments (see left panel) and first principles calculations. It was found that the high stability of the cluster 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.



STM image (left) of a monatomic-layered platinum cluster disk, Pt₃₀, constructed on the Si(111) surface. Schematic image (right) of two-dimensional charge polarization; the Pt-5d electrons are distributed out of the cluster, so that the centre and the periphery of the cluster are charged positively and negatively, respectively.

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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 , 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 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_N^+ 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 $3 \times 10 \text{ mm}^2$ 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 $\Omega \text{ cm}$) 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 $4 \times 4 \times 1$ 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

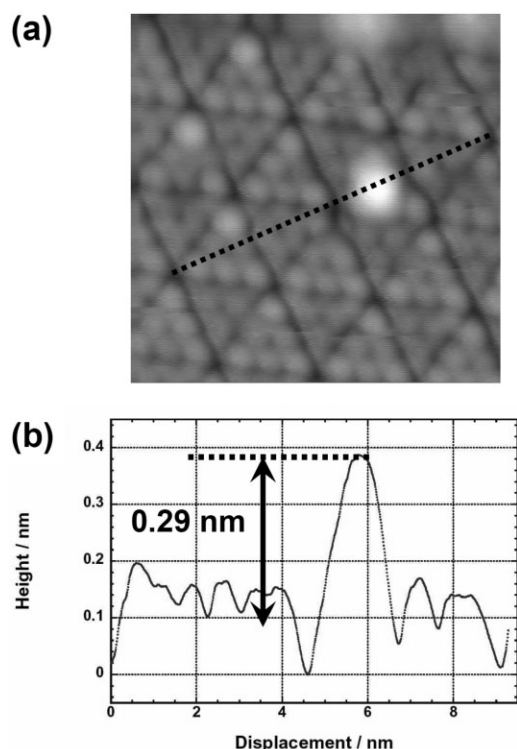


Figure 1 (a) STM image of a uni-sized platinum cluster disk, Pt_{30} , deposited on the FH of the Si(111) surface and (b) trace of the STM probe along the broken line indicated in panel a. The STM image was measured at a temperature of 77 K at a constant tunnelling current of 1.0 nA by applying the bias 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.

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)- 7×7 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 Pt_{30} 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)- 7×7 surface if the 7×7 reconstructed structure was maintained even after the cluster deposition. Figure 2 shows the correlation between the apparent height and the deposition site of each Pt_{30} disk. There appears no correlation between the height and the deposition site. Furthermore, no preferential deposition site is observed.

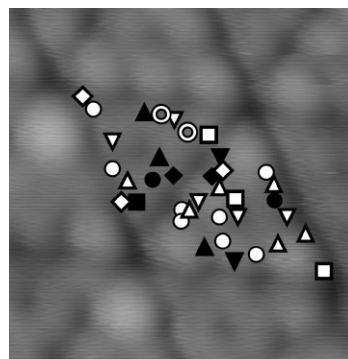


Figure 2 Correlation between the apparent height and the deposition site obtained from STM images measured for 36 Pt_{30} cluster disks deposited on the Si(111) surface. The marks denote the deposition sites with the height of 0.26 (○), 0.27 (◇), 0.28 (□), 0.29 (△), 0.30 (▽), 0.31 (⊙), 0.32 (●), 0.33 (◆), 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 Pt_{30} 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

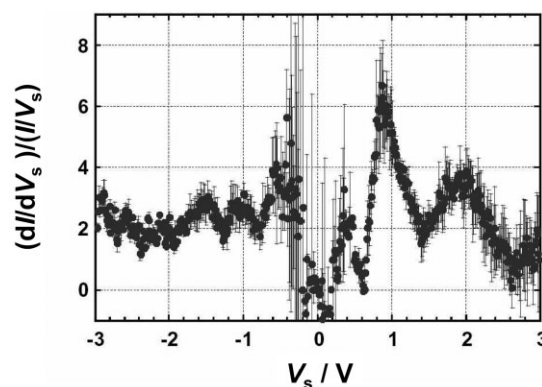


Figure 3 Space-resolved tunnelling spectrum measured over a Pt_{30} cluster disk deposited on the FH of the Si(111) surface shown in Fig. 1, where the STM probe was located above the centre of this cluster disk; I and V_s are the tunnelling current and the bias voltage applied to the sample with respect to the STM probe. The spectrum was measured at a temperature of 77 K.

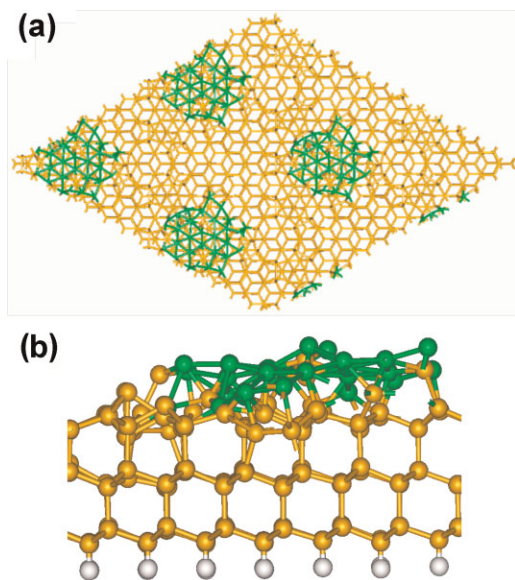


Figure 4 (online colour at: www.pss-b.com) (a) Top and (b) side views of the geometry of Pt_{30} optimized by means of first principles calculations, where the cluster is deposited on the centre of the UFH of the $\text{Si}(111)-7 \times 7$ surface. The green, yellow and grey balls indicate Pt, Si and H atoms, respectively.

was found that the electrons in the occupied level at 1.5 eV below the chemical potential are distributed in a diameter of 2 ± 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 Pt_{30} 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_{ad} , of this cluster is 44.54 eV (=1.485 eV per atom), which was calculated according to

$$E_{\text{ad}} = E_{\text{Si}} + E_{\text{Pt}} - E_{\text{Pt@Si}}, \quad (1)$$

where E_{Si} , E_{Pt} and $E_{\text{Pt@Si}}$ are total energies of the clean $\text{Si}(111)-7 \times 7$ surface, the isolated and the supported Pt_{30} , 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 states (PDOS) projected onto the Pt-5d, Si-3s and Si-3p atomic orbitals of the optimized Pt_{30} disk deposited on the FH of the $\text{Si}(111)-7 \times 7$ surface. In PDOS, the Pt-5d states are dominated from -1.7 to 0.8 eV, as compared to the Si-3s and Si-3p states. Several peaks at -1.5 , -1.08 , -0.84 , -0.44 , -0.17 , 0.08 , 0.25 , 0.47 and 0.8 eV are pronounced within the Pt states dominated region. Most of peaks in the occupied energy

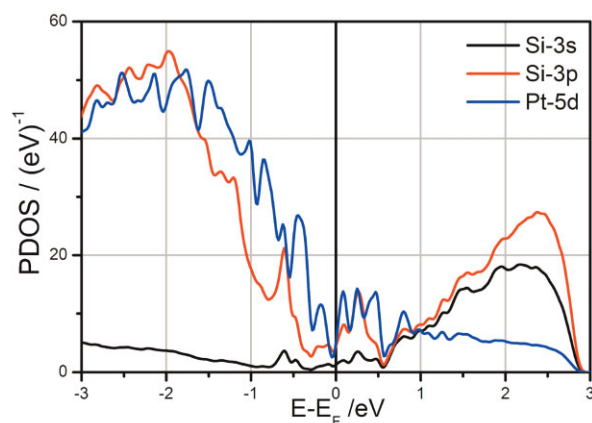


Figure 5 (online colour at: www.pss-b.com) Partial densities of electronic states (PDOS) of Pt_{30} calculated by first principles calculations, where the cluster is deposited on the centre of the FH of the $\text{Si}(111)-7 \times 7$ surface. The energy is measured with respect to the Fermi energy, E_{F} .

range are quite comparable with the normalized differential conductance measured in the experiments, while peaks in the unoccupied range are deviated as a result of predicting the underestimated energy band gap by density functional theory [25]. Hence, most of features from electronic structure calculations reproduce our experimental results. The conductance, $dI/dV_{\text{s}}/(I/V_{\text{s}})$, around $V_{\text{s}} = 0$ is significantly reduced and the peaks are observed at almost the same energy positions as calculated (see Fig. 3). Similar trend was obtained in PDOS calculated for Pt_{30} deposited on the UHF. Furthermore, Fig. 5 reveals the strong interaction between the Pt-5d orbital and the Si-3s and 3p orbitals. By analysis of PDOS, it was found that they are constructed by hybridization of the Pt-5d, Si-3s and Si-3p atomic orbitals so as to form the Pt–Si bond, and that the strong Pt–Si bonding originates from electron transfer from the Pt-5d atomic orbital to the Si-3s and Si-3p ones. We calculated the excess and depletion of the charge densities, $\delta\rho$, according to

$$\delta\rho = \rho(\text{Pt@Si}) - \rho(\text{Pt}) - \rho(\text{Si}), \quad (2)$$

where $\rho(\text{Pt})$, $\rho(\text{Si})$ and $\rho(\text{Pt@Si})$ are the total charge densities of the Pt_{30} cluster, the Si surface and the combined system, respectively. Figure 6 shows the charge density differences of the Pt_{30} disk deposited on the FH of the $\text{Si}(111)-7 \times 7$ surface to understand the charge transfer mechanism in the system. The excess electrons are distributed in between the Pt_{30} disk and the Si surface, while the top of the Pt_{30} disk depletes electrons. The same kind of electron transfer was discernible in the calculations for the Pt_{30} 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 Pt_{30} placed

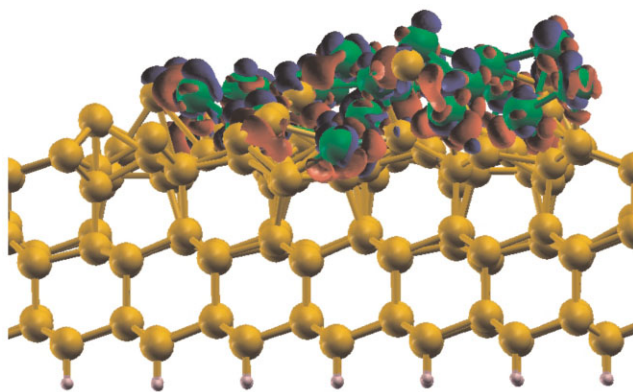


Figure 6 (online colour at: www.pss-b.com) The excess and depletion charge densities of Pt_{30} on the centre of the FH of the $\text{Si}(111)-7 \times 7$ surface (side view). The blue and red isosurfaces correspond to -0.165 and $+0.165$ electrons nm^{-3} , respectively. The green, yellow and pink balls indicate Pt, Si and H atoms, respectively.

on the Si surface as shown in Figs. 1, 4 and 6. The monatomic-layered geometry on the Si surface is stable as the adsorption energy of ~ 45 eV. This configuration has the largest bonding energy between the Pt and Si atoms, because it has the largest number of the Pt–Si bonds, which was calculated to be the strongest in any bonds of this system. The complete destruction of the 7×7 atomic configuration of the Si surface under the cluster disk [7] is also reproduced by the calculation as shown in Figs. 4 and 6. This is another aspect of the large excess energy in the formation of the strong bonding between the Pt and Si atoms.

5.2 Deposition site As shown in Fig. 2, the Pt_{30} disks are placed randomly on the $\text{Si}(111)$ surface. Therefore, there are no preferable sites for the cluster deposition. The calculations support this finding as the adsorption energies on the FH and UHF differ only by $\sim 3\%$. This uniformity in the adsorption energy originates from the amorphous structure under the cluster disk due to the complete destruction of the 7×7 configuration. Therefore, the following scheme seems to proceed during the cluster deposition by the cluster impact under the present experimental condition: Right after the cluster ion touches the Si surface in the cluster impact process, the cluster could move on the surface shorter than ~ 5 nm from the landing position [7] by the gain of the high excess energy as a result of the Pt–Si bond formation as well as the collision energy, and finally the cluster is fixed on the surface as a cluster disk with no further surface migration. This scheme can be extended to a soft-landing condition, that is the collision energy of the cluster ion as low as ~ 30 meV (thermal energy at 300 K): The cluster is fixed also as a cluster disk with complete destruction of the Si surface even at the thermal energy, because the excess energy (~ 45 eV) due to the Pt–Si bond formation is still enough for this geometry change.

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 $\text{Si}(111)$ 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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