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Pinning of size-selected Pd nanoclusters on graphite

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The production of stable cluster arrays on smooth surfaces has several potential technological applications. We report a study of the pinning of size-selected palladium nanoclusters on the graphite surface. The clusters formed during gas aggregation in vacuum are projected with sufficient kinetic energy to create a defect in the graphite surface. The energy necessary to create such an immobilizing defect is investigated as a function of the palladium cluster size. The palladium pinning energy is found to deviate from the simple binary collision model as appropriate to previously reported silver and gold results. This finding is in agreement with the deviation of nickel clusters and points to the influence of the interatomic cluster bonding on the mechanics of the collision. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2337288]

I. INTRODUCTION

The deposition of atomic clusters on surfaces[1–8] is not only of fundamental interest but also highly relevant to possible technological applications. Much research has already been devoted to the optical,[9,10] magnetic,[11] and catalytic[12,13] properties of clusters, which are strongly size dependent.[14,15] There are several methods to produce size-selected nanoclusters,[16] such as the gas aggregation source combined with a mass selector, which offers accurate size selection and control of deposition energy[17–19] while the soft landing of clusters at low deposition energies avoids fragmentation, fast cluster diffusion and aggregation at room temperature on smooth surfaces such as graphite hinders the observation of single clusters,[20] so that cryogenically cooled surfaces are required.[21] As the use of nanoclusters in chemical or catalytical reactions often takes place at elevated temperatures, this route restricts the potential technological employment of such systems.

Arrays of size-selected clusters, which are stable at room temperature, can be created at higher impact energies as demonstrated by Carroll *et al.*[22] using the pinning technique; the clusters are immobilized on the substrate at the point of landing by the creation of a surface defect in the uppermost graphite layer. It was suggested that the dangling bonds of this defect result in the binding of the cluster.[23] This is analo-gous to cluster pinning by defects on oxide surfaces.[24,25] The energy to produce such a defect was also shown to scale linearly with the mass of the cluster, consistent with a binary elastic collision model. An investigation into the universality of this binary collision model by Di Vece *et al.*[26] showed that the pinning energy of gold clusters is also well described by a linear relation. However, nickel clusters were found to deviate somewhat from the expected linear relation. In the Periodic Table, nickel is located in the column before that of the noble metals. Therefore the question arises whether the behavior of nickel is caused by its different electronic state as compared to silver and gold. To explore this idea further, we have selected an element from the same column, with similar electronic properties. To exclude mass effects we chose palladium, as it lies next to silver, which means that the effect of the mass difference can be neglected. Palladium is also a very important material for catalysis[27] and potentially for hydrogen storage,[28] and therefore this investigation may have a technological importance.

Specifically, we present an experimental scanning tunneling microscopy (STM) study of size-selected Pd_N clusters (N=50, 100, 150, 200, and 250), deposited onto a graphite surface [highly oriented pyrolytic graphite (HOPG)] at room temperature and at different incident energies. We compare our results with the data previously reported for silver clusters[22] and gold and nickel clusters.[26]
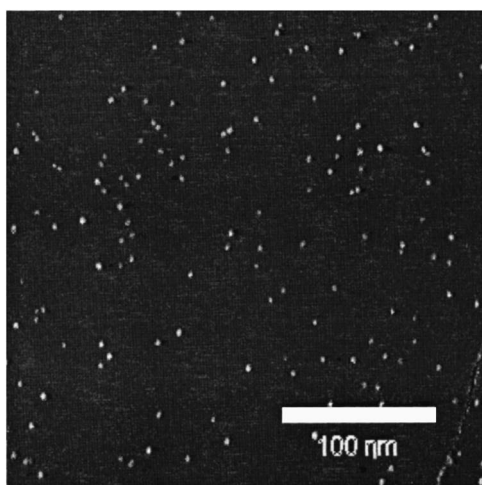
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FIG. 1. STM image (300×300 nm^2) of Pd$_{150}$ clusters deposited on graphite at 1.8 keV, obtained with a surface bias voltage of 300 mV and tunnel current of 0.1 nA.
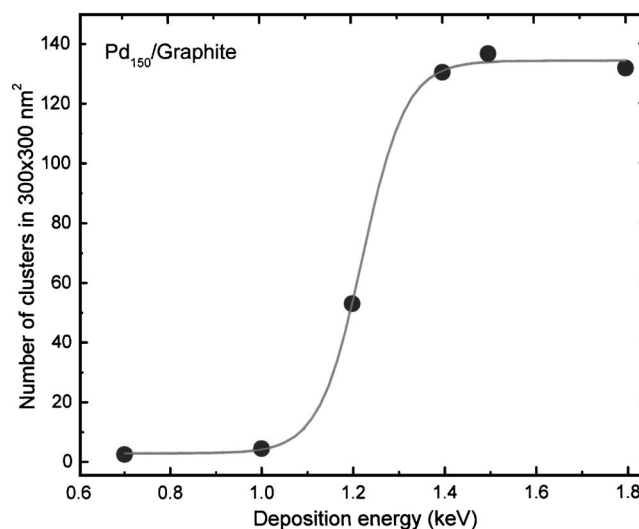

FIG. 2. Density of Pd$_{150}$ clusters deposited on graphite as a function of impact energy. The midpoint between the two plateaus defines the pinning energy.

II. EXPERIMENT

Size-selected Pd clusters were produced in a magnetron sputtering, gas aggregation cluster source, described in detail elsewhere.[18,19] The background pressure in the cluster source is $\sim 10^{-8}$ mbar and the working pressure, after introducing argon and helium, is $\sim 10^{-6}$ mbar. A rf argon plasma sputters a target, in this case palladium, creating a cloud of hot atoms, which condense to clusters in a flowing stream of cold He gas. The positively charged clusters in the beam are accelerated and focused by a set of ion optics and then mass selected by a lateral time of flight mass selector, described elsewhere.[17] The typical resolution of the mass selector ($\Delta M / M$) is about 5%. The cluster deposition energy is controlled by the voltage applied to the sample and the coverage is determined by measuring the ion current and deposition time. The kinetic energy range used during these experiments was 0.2–2.5 keV.

Before introducing into the vacuum system, the HOPG samples were prepared by cleaving in air. STM imaging of the cluster samples was performed in air at room temperature a few days after deposition, using a Digital Instruments multimode STM. Typical voltage and current parameters were 300 mV and 0.1 nA. Mechanically cut Pt/Ir tips were used and STM images were taken in constant current mode. The images were analyzed using a software package scanning probe image processor (SPIP), Image Metrology.

III. RESULTS AND DISCUSSION

To determine the experimental pinning energy of the size-selected palladium clusters on graphite, we measured the average density of the deposited clusters at different kinetic energies. Figure 1 shows a typical STM image of pinned clusters obtained for Pd$_{150}$ at 1.8 keV. By contrast, when clusters are not pinned, i.e., at low impact energies, they diffuse freely on the graphite surface until they reach a defect or a step edge where they are immobilized.

In Fig. 2 the density of detected Pd$_{150}$ clusters is shown as a function of the deposition energy. The plotted densities

are obtained by averaging over different areas on the sample. This procedure was applied to clusters with sizes $N = 50$, 100, 150, 200, and 250. In each case at low energies, the cluster density is almost zero, as the clusters are not pinned. As the kinetic energy increases, a sharp rise can be observed, until a plateau value is reached. The pinning threshold is taken as the midpoint between the two plateaus,[22] and thus the experimental pinning energy is obtained as a function of the cluster size, Fig. 3. Tip convolution effects make it difficult to ascertain possible changes in the precise three-dimensional morphology of the clusters as a function of deposition energy; scanning transmission electron microscopy offers one attractive approach to this problem.[29] The collision of a metal cluster, of sufficient kinetic energy, with the graphite surface displaces a carbon atom from its initial position to an interstitial site. The defect then binds the cluster to the sur-
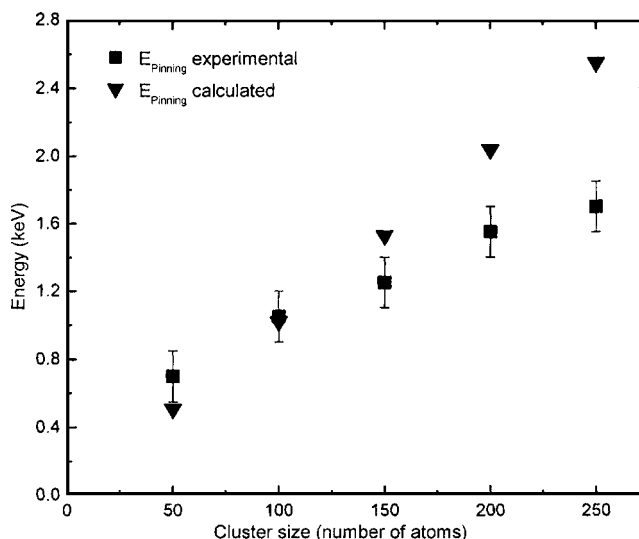

FIG. 3. Experimental pinning energy of Pd$_N$ clusters on graphite as function of cluster size (squares). The triangles represent the values obtained by extension of the experimental results for silver clusters according to the binary elastic collision model.

TABLE I. Bulk lattice constants of relevant metals (Refs. 34–37).

Metal	Lattice constant (nm)
Ag	0.409
Au	0.408
Pd	0.389
Ni	0.352

face, preventing cluster diffusion. At high temperatures the clusters are released and aggregate together.[30] A simple model for the pinning process of Ag_N clusters on graphite was proposed by Carroll *et al.*[22] to account for the linear relation between pinning energy and cluster size obtained from both experiment and detailed molecular dynamics simulations.[31–33] For a binary elastic collision model in which the energy and momentum are conserved, they obtained the relationship

$$E_P = N \frac{M_{Ag} E_T}{4 M_C}, \qquad (1)$$

where E_P is the pinning energy, E_T is the energy which has to be transferred to displace a carbon atom, and M_{Ag} and M_C are the masses of a silver and a carbon atom, respectively. This model was also successfully extended to gold clusters.[26] Figure 3 shows the pinning energies for the palladium clusters with the values calculated by extending the silver model. Good agreement between the model and experiment is observed for the small sizes, but at large sizes the experimental data show a significant deviation from the linear relationship. An even stronger deviation from linearity was observed in the case of nickel clusters[26] and suggests the possibility that this behavior is associated with the electronic structure of the group X clusters.

A quantitative explanation of the difference between the precise pinning behavior of gold and silver clusters, on one hand, and nickel and palladium clusters, on the other, awaits a detailed theoretical treatment. Meanwhile, in Table I we give the lattice constants of the considered elements. The lattice constants of gold and silver in the crystalline solid state are almost identical, while that of nickel is 15% smaller. The lattice constant of palladium lies between the noble metals and nickel. We see that there is a qualitative empirical correspondence between the degree of deviation of the measured pinning energy curve and the lattice constant. Of course, the lattice constant is itself a manifestation of the interatomic bonding in the cluster, which is likely to influence the plastic deformation of the shape of the cluster upon impact with the surface.

Further experiments with clusters of different metallic elements would be able to establish the generality of the posited link between pinning energy and lattice constant emerging from this work. From a technological point of view, the preparation of monodispersed films of size-selected Pd_N ($N = 50-250$) clusters has been established, opening the way for experimental studies of the cluster size dependence of, e.g., hydrogen storage and chemical reactivity on an industrially relevant support, graphite.

[1] C. L. Cleveland and U. Landman, Science **257**, 355 (1992).
[2] V. Kresin, Phys. Rep. **220**, 1 (1992).
[3] M. Brack, Rev. Mod. Phys. **65**, 677 (1993).
[4] A. Perez, P. Melinon, V. Dupuis *et al.*, J. Phys. D **30**, 709 (1997).
[5] P. Jensen, Rev. Mod. Phys. **71**, 1695 (1999).
[6] C. Binns, Surf. Sci. Rep. **41**, 1 (2001).
[7] C. Bostedt, T. Van Buuren, J. M. Plitzko, T. Moller, and L. J. Terminello, J. Phys.: Condens. Matter **15**, 1017 (2003).
[8] S. Pratontep, P. Preece, C. Xirouchaki, R. E. Palmer, C. F. Sanz-Navarro, S. D. Kenny, and R. Smith, Phys. Rev. Lett. **90**, 055503 (2003).
[9] L. Patrone, D. Nelson, V. I. Safarov, M. Sentis, W. Marine, and S. Giorgio, J. Appl. Phys. **87**, 3829 (2000).
[10] G. Ledoux, J. Gong, F. Huisken, O. Guillois, and C. Reynaud, Appl. Phys. Lett. **80**, 4834 (2002).
[11] M. Jamet, W. Wernsdorfer, C. Thirion, D. Mailly, V. Dupuis, P. Melinon, and A. Perez, Phys. Rev. Lett. **86**, 4676 (2001).
[12] U. Heiz, R. Sherwood, D. M. Cox, A. Kaldor, and J. T. Yates, Jr., J. Phys. Chem. **99**, 8730 (1995).
[13] A. Sanchez, S. Abbet, U. Heiz, W. D. Schneider, H. Hakkinen, R. N. Barnett, and U. Landman, J. Phys. Chem. A **103**, 9573 (1999).
[14] A. P. Alivisatos, J. Phys. Chem. **100**, 13226 (1996).
[15] R. L. Johnston, Philos. Trans. R. Soc. London, Ser. A **356**, 212 (1998).
[16] W. A. de Heer, Rev. Mod. Phys. **65**, 611 (1993).
[17] B. von Issendorff and R. E. Palmer, Rev. Sci. Instrum. **70**, 4497 (1999).
[18] I. M. Goldby, L. Kuipers, B. Issendorf, and R. E. Palmer, Rev. Sci. Instrum. **68**, 3327 (1997).
[19] P. Pratontep, S. J. Carrol, C. Xirouchaki, M. Streun, and R. E. Palmer, Rev. Sci. Instrum. **76**, 045103 (2005).
[20] L. Bardotti, P. Jensen, A. Houreau, M. Treilleux, and B. Cabaud, Phys. Rev. Lett. **74**, 4694 (1995).
[21] A. Bettac, L. Koller, V. Rank, and K. W. Meiwes-Broer, Surf. Sci. **402**, 475 (1998).
[22] S. J. Carroll, S. Pratontep, M. Streun, R. E. Palmer, S. Hobday, and R. Smith, J. Chem. Phys. **113**, 7723 (2000).
[23] R. Smith, C. Nock, S. D. Kenny, J. J. Belbruno, M. Di Vece, S. Palomba, and R. E. Palmer, Phys. Rev. B **73**, 125429 (2006).
[24] X. Tong, L. Benz, S. Crétien, P. Kemper, A. Kolmakov, H. Metiu, M. T. Bowers, and S. K. Buratto, J. Chem. Phys. **123**, 204701 (2005).
[25] L. Benz, X. Tong, P. Kemper, H. Metiu, M. T. Bowers, and S. K. Buratto, J. Phys. Chem. B **110**, 663 (2006).
[26] M. Di Vece, S. Palomba, and R. E. Palmer, Phys. Rev. B **72**, 073407 (2005).
[27] C. M. Grimaud, D. Radosavkic, S. Ustaze, and R. E. Palmer, Appl. Surf. Sci. **178**, 1 (2001).
[28] J. M. Bernis and L. F. Dahl, J. Am. Chem. Soc. **119**, 4545 (1997).
[29] Z. Li, J. Yuan, Y. Chen, R. E. Palmer, and J. P. Wilcoxon, Adv. Mater. (Weinheim, Ger.) **17**, 2885 (2005).
[30] F. Yin, C. Xirouchaki, Q. Guo, and R. E. Palmer, Adv. Mater. (Weinheim, Ger.) **17**, 731 (2005).
[31] S. D. Kenny, A. P. Horsfield, and H. Fujitani, Phys. Rev. B **62**, 4899 (2000).
[32] G. M. Wang, J. J. BelBruno, S. D. Kenny, and R. Smith, Surf. Sci. **541**, 91 (2003).
[33] G. M. Wang, J. J. BelBruno, S. D. Kenny, and R. Smith, Phys. Rev. B **69**, 195412 (2004).
[34] A. Maeland and T. B. Flanagan, Can. J. Phys. **42**, 2364 (1964).
[35] L. G. Liu and W. A. Bassett, J. Appl. Phys. **44**, 1475 (1973).
[36] A. Taylor, J. Inst. Met. **77**, 585 (1950).
[37] C. N. Rao and K. K. Rao, Can. J. Phys. **42**, 1336 (1964).