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Atomic process of epitaxial growth of gold on magnesium oxide studied by cross-sectional time-resolved high-resolution electron microscopy

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Gold was vacuum deposited on a (001) surface of magnesium oxide inside a high-resolution electron microscope. The atomic process of epitaxial growth was observed cross sectionally *in situ* with time-resolved high-resolution transmission-electron microscopy. Various types of growth phenomena, such as nucleation center formation, structural fluctuations, shape modulation, secondary nucleation, and coalescence, were analyzed in real space at a spatial resolution of 0.2 nm and a time resolution of 1/60 s. It was found that a central corner of a cluster is truncated and constructed repeatedly during the growth. [S0163-1829(97)50240-2]

I. INTRODUCTION

Gas phase epitaxial growth relating to formation of interfaces, thin films, and atomic clusters is a most important subject in surface science, solid state physics, and materials science.[1,2] Various structural analyses, such as transmission and scanning electron microscopy, low-energy electron diffraction, reflection high-energy electron diffraction, and scanning probe microscopy, have been attempted to study the epitaxial growth. In particular, conventional transmission electron microscopy (CTEM) is a most useful method. It is known that each elemental process of epitaxial growth was analyzed by plan-view CTEM of *in situ* vacuum deposition in electron microscopes.[3–8] Many unresolved problems, however, still remain in the studies of the atomic process of the epitaxial growth. Further advanced techniques are required for electron microscopy although many complicated improvements of the specimen chambers, the objective lenses, the specimen holders, and the evaporation sources have been attempted for the *in situ* vacuum depositions.[3–8] Takayanagi *et al.* demonstrated high-resolution transmission electron microscopy (HRTEM) of the nucleation process of gold on an amorphous carbon film during *in situ* vacuum deposition.[9] This work suggested that *in situ* atomisitic observation will give substantial information for the elucidation of the growth process. A remaining problem is how to observe crystalline/crystalline interfaces of less than a few nanometers thickness and/or width during the epitaxial growth. Such interfaces cannot be directly observed by plan-view HRTEM or scanning probe microscopy (SPM). Interfaces that are internal two-dimensional structures and exist deeper than ten or more atomic layers from surfaces cannot be observed by SPM. Plan-view TEM also cannot directly observe interface structures, because images of an interface and materials that are located beside the interface are overlapped. The atomic arrangement cannot be analyzed from such overlapped images. Cross-sectional time-resolved HRTEM (TRHRTEM) is thus the optimum method to observe directly the atomic arrangements of such interfaces as shown previously by Kizuka, Kachi, and Tanaka.[10]

The purpose of the present study is to elucidate the atomic process of epitaxial growth during vacuum deposition by development of cross-sectional TRHRTEM.

II. EXPERIMENTAL PROCEDURES

Single crystalline magnesium (MgO) films for growing substrates were prepared by vacuum deposition. MgO of 99.99% purity was evaporated by electron-beam heating and deposited on air-cleaved (001) surfaces of sodium chloride (NaCl) in a work chamber evacuated to 10^{-6} Pa using a turbo molecular pump and an ion pump. The substrate temperature was 300 °C. The deposition thickness and the deposition rate were estimated to be 18 nm and 9 nm/min, respectively, as measured using a quartz-crystal monitor. The deposited films were separated from the substrates by dissolving in distilled water and mounted on grids for electron microscopy.

Figure 1 is an illustration of the specimen chamber of a 200-kV high-resolution electron microscope (JEOL, JEM-2010) for *in situ* vacuum deposition and cross-sectional time-resolved high-resolution observation. A MgO substrate was

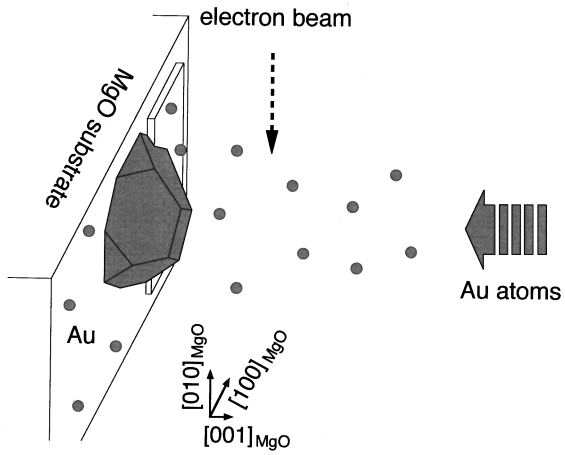

FIG. 1. Illustration of the present specimen chamber of a 200-kV high-resolution electron microscope for *in situ* vacuum deposition and cross-sectional time-resolved high-resolution observation.

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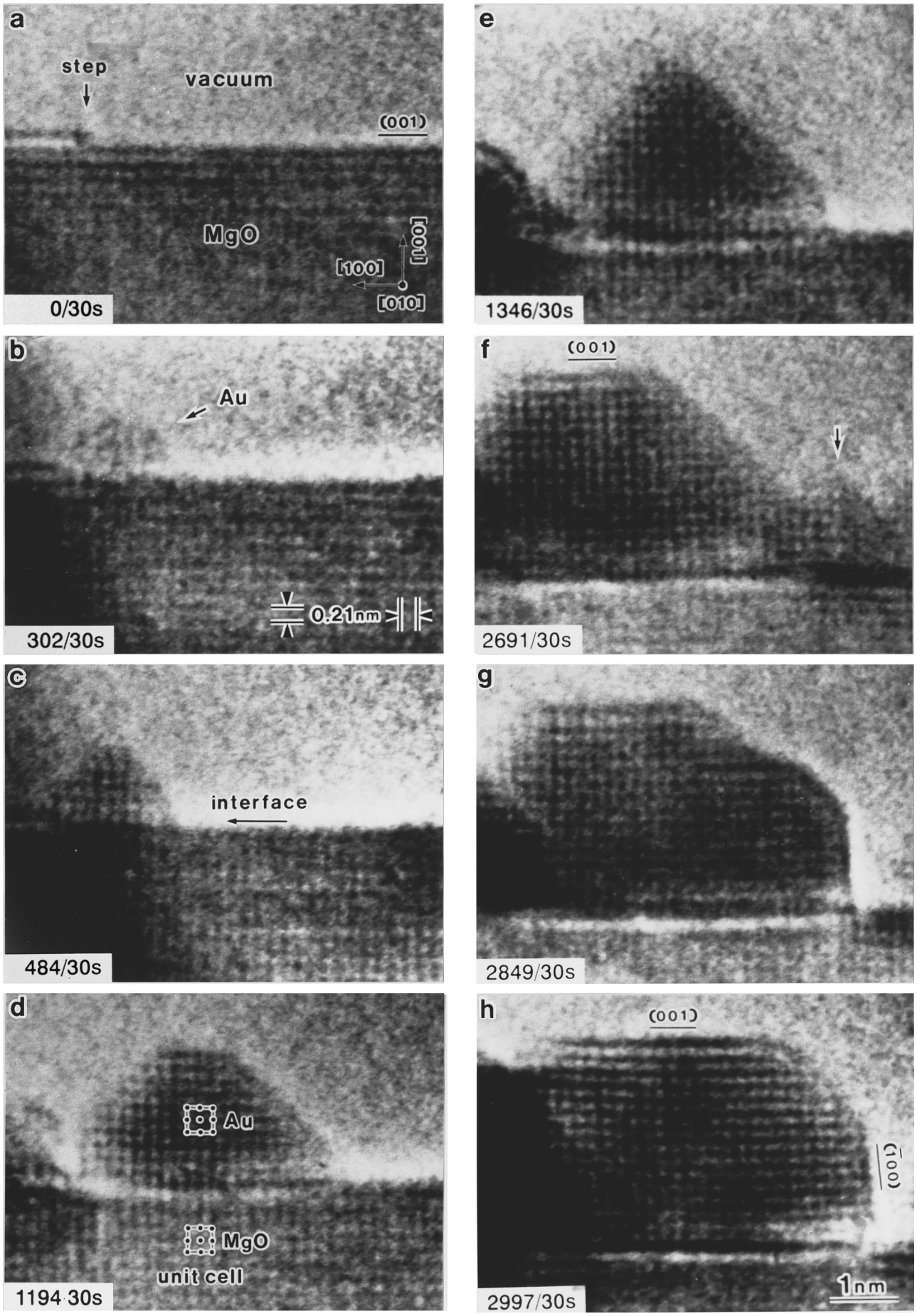

FIG. 2. Time-sequence series of high-resolution images of the epitaxial growth process of one Au cluster on a (001) MgO surface.

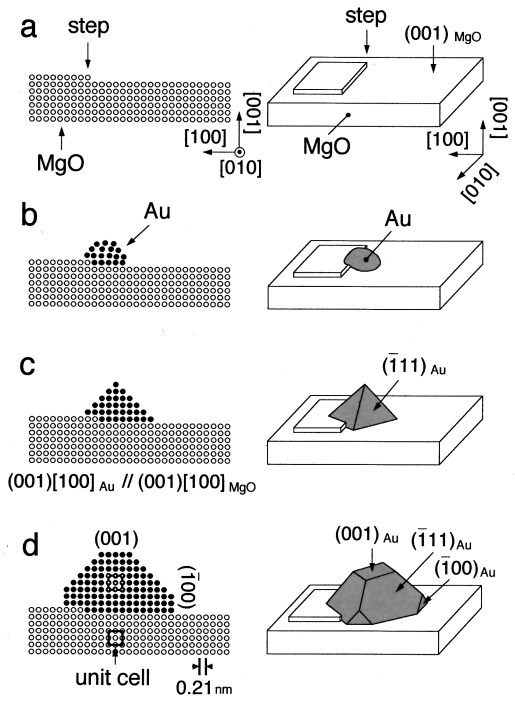

FIG. 3. Atomic arrangements (left side) and illustration of the growth process (right side) for Figs. 2(a)–2(d).

set in a specimen holder for *in situ* vacuum deposition. High-resolution observations were simultaneously carried out at the electron beam irradiation density of 3×10^5 A/m^2. The surfaces of the substrate were cleaned by the nanometer-scale electron beam processing.[11] The electron-beam irradiation density during the electron-beam processing was five times larger than that during the observations, that is, 1.5×10^6 A/m^2. Gold (Au) was vacuum deposited on an (001) surfaces of the MgO substrates at room temperature in a specimen chamber of the electron microscope.[12] The pressure in the chamber was 2×10^{-5} Pa. The growing process was *in situ* observed cross sectionally by TRHRTEM at a spatial resolution (point-to-point) of 0.2 nm and at a time resolution of 1/60 s using a high-sensitivity TV camera and a video tape recorder.[10]

III. RESULTS AND DISCUSSION

Figure 2 shows a time-sequence series of high-resolution images of the epitaxial growth process of Au on a $(001)_{MgO}$ surface. Atomic arrangements and illustrations of the growth process for Figs. 2(a)–2(d) are shown in Fig. 3. The atomic arrangement was determined by the comparison with the image simulations using an established multislice program.[13] It is surmised that behavior of the Au cluster is dependent on the size of the cluster.[14–16] Figure 4 shows the number of constituent atoms in the Au cluster in Fig. 2 as a function of deposition time. The Au cluster in Figs. 2(b)–2(e) shows symmetrical shape with respect to the (100) plane. Symmetrical shapes with respect to the $[001]_{MgO}$ axis were assumed as shown in Fig. 3 for the estimation of the number of the constituent atoms. The slope of the number increases with time as shown in Fig. 4. The increase may be attributed to the changes of sticking probability of Au atoms impinging on the MgO substrate, or the increase of deposition rate. The

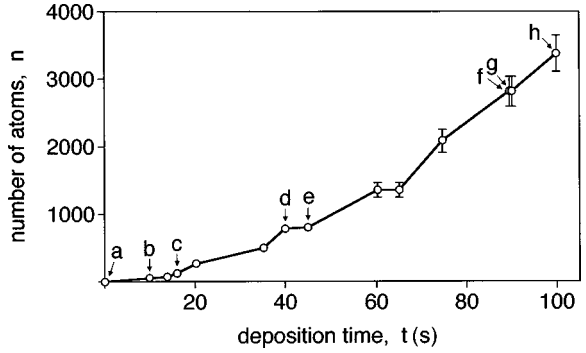

FIG. 4. The number of constituent atoms in the Au cluster in Fig. 2 as a function of deposition time. Times at *a*-*h* correspond to times at *a*-*h* in Fig. 2.

behavior should be analyzed as a function of the number of constituent atoms in the cluster instead of the deposition time as follows.

First, a step of one atomic height is observed on the $(001)_{MgO}$ clean surface before the deposition [Fig. 2(a); an arrow]. No contamination is observed during the observation though the electron-beam density is not sufficiently large to change the surface structure of the substrate. One Au cluster as a nucleation center forms on the step at the beginning of the deposition and no Au cluster forms on terrace [Fig. 2(b)]. This shows that nucleation probability increases at the step. This may be due to the collisions of Au atoms diffusing along the step. It is well known that steps become nucleation sites similarly to precipitates and points defects.[1–2] A problem has been where the nucleation takes place, for example, the top of a step, lower part of a step, or astride a step. In the present epitaxial growth, it is clear the nucleation occurs astride the step. The number of the constituent atoms in the cluster in Fig. 2(b) is less than 60. The cluster shows structural fluctuation. The present structural fluctuation is similar to those observed after vacuum deposition in Au clusters supported on amorphous silicon oxide[17,18] and MgO (Refs. 10,19,20). The orientation relationship between the present cluster and the substrate also changes frequently. The structural fluctuation stops and an epitaxial orientation, $(001)\times[100]_{Au}\|(001)[100]_{MgO}$ emerges when the number of atoms increases to more than 90 [Fig. 2(c)]. Kizuka, Kachi, and Tanaka previously observed by TRHRTEM the interface between Au clusters and MgO substrates during the structural fluctuation.[10] They investigated the relation between the interface structure and the duration time. This work showed that the duration time of the $(001)[100]_{Au}\|(001)[100]_{MgO}$ epitaxial interface was the longest; the (001) epitaxial interface was the most stable. The external shape of the present cluster transforms to a tetragonal pyramid surrounded with a $(001)_{Au}\|(001)_{MgO}$ interface and four $\{111\}_{Au}$ surfaces. The epitaxial orientation is maintained even when the tetragonal pyramid grows [Figs. 2(c)–2(d)]. Obviously, the growth mode of the present Au/MgO system is an island growth mode (Volmer-Weber mode). A top corner of the cluster is truncated with a $(001)_{Au}$ plane and four corners at the bottom are also truncated with $(001)_{Au}$ and $(010)_{Au}$ planes [Fig. 2(d)]. The top corner then forms again. Such shape modulation from tetragonal pyramid to truncated tetragonal pyramid or the inverse appears repeatedly [Figs. 2(c)–2(f)]. This is

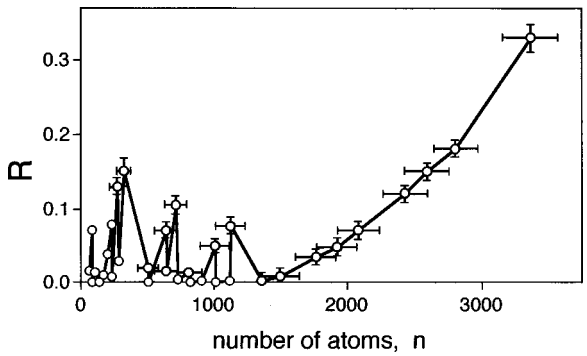

FIG. 5. Variation of ratio R relating to the repeated process of truncation and construction of the top corner as a function of the number of the atoms. R is defined as the ratio of $A_{\{100\}}\|A_{\{111\}}$, where $A_{\{100\}}$ and $A_{\{111\}}$ are the total area of five {100} surfaces and the total area of four {111} surfaces of the cluster, respectively.

clearly found with the present time-resolved observation of one cluster. Figure 5 shows the variation of a ratio R relating to the repeated process of truncation and construction of the top corner as a function of the number of atoms. The R is defined as $A_{\{100\}}\|A_{\{111\}}$, where $A_{\{100\}}$ and $A_{\{111\}}$ are the total area of five {100} surfaces and the total area of four {111} surfaces of the cluster, respectively. The R fluctuates, that is, the repeated process continues when the number of the atoms is less than 1400. One repeated process completes when the R is zero. The number of the repeated process is five in the present observation as shown in Fig. 5. It is considered that the truncation takes place in order to reduce the total surface energy of the cluster.[21] On the other hand, the construction of the top corner after the truncation will result from the total energy reduction of the cluster by the decrease of Au/MgO interface and strained regions, because, if the impinging and diffusing atoms bond with the bottom of the cluster near the interface and do not move, the area of the interface increase and the interface energy and misfit strain energy also increase. As a result, the atoms in the strained regions decrease and the atoms near the top corner increase. The repeated process may suggest that the total energy of the truncated cluster is similar to that of a nontruncated cluster when the number of atoms in the cluster is less than 1400. The R decreases gradually, showing that the cluster does not grow along the direction parallel to the $[001]_{MgO}$ after the number of atoms is more than 1400. A new Au cluster forms in the neighborhood, that is, secondary nucleation occurs [Fig. 2(f)]. The two clusters coalesce into one when the deposition further continues [Fig. 2(g)]. The epitaxial orientation at the interface is retained even after the coalescence. A well-defined crystal habit appears in the cluster again after the coalescence [Fig. 2(h)]. Such secondary nucleation was reported by Honjo and Yagi for the epitaxial growth process of the Au/MgO system.[22] They pointed out that the secondary nucleation occurred when nucleation sites appeared again in areas of the substrate reexposed due to moving of deposited clusters at colescence. However, in the present work, the secondary nucleation takes place before the coalescence. No step as nucleation site is observed on the surface. Point defects created on the MgO surface during the deposition may be a nucleation site.

In conclusion, the atomic process of the epitaxial growth, such as the nucleation center formation, the structural fluctuation, the repeated process of the truncation and construction of the corner, secondary nucleation and coalescence can be analyzed as functions of the number of the constituent atoms of one cluster. The present *in situ* observation on an atomic scale and at 1/60 s time-resolution will give us new and quantitative information about epitaxial growth and other phenomena relating to clusters and/or surfaces. The cross-sectional TRHRTEM is a new method to study atomic process of gas phase epitaxial growth.

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[1] D. W. Pashley, Adv. Phys. **5**, 173 (1956).
[2] R. Kern, G. Le Lay, and J. J. Metois, in *Current Topics in Materials Science*, Vol. 3, edited by E. Kaldis (North-Holland, Amsterdam, 1979), p. 132.
[3] T. A. Maclauchlan, R. S. Sennett, and G. S. Scott, J. Res. A **28**, 530 (1950).
[4] G. A. Bassette, in *Proceedings of the European Regional Conference on Electron Microscopy, Delft*, (North-Holland, Amsterdam, 1961), p. 270.
[5] D. W. Pashley, M. J. Stowell, M. H. Jacobs, and T. J. Law, Philos. Mag. **10**, 127 (1964).
[6] H. Poppa, J. Vac. Sci. Technol. **2**, 42 (1965).
[7] M. J. Stowell, Thin Solid Films **12**, 341 (1972).
[8] G. Honjo, K. Takayanagi, K. Kobayashi, and K. Yagi, Phys. Status Solidi A **55**, 353 (1979).
[9] K. Takayanagi, Y. Tanishiro, K. Kobayashi, K. Akiyama, and K. Yagi, Jpn. J. Appl. Phys., Part I **26**, 1957 (1987).
[10] T. Kizuka, T. Kachi, and N. Tanaka, Z. Phys. D **26**, S58 (1993).
[11] T. Kizuka and N. Tanaka, Philos. Mag. A **71**, 631 (1995).
[12] The attachment for vacuum deposition in the electron microscope was produced by Katsuyoshi Kumazawa at the Workshop of the Department of Applied Physics at Nagoya University.
[13] K. Ishizuka, Ultramicroscopy **5**, 55 (1980).
[14] *Microclusters*, edited by S. Sugano, Y. Nishina, and S. Ohnishi (Springer, Berlin, 1987).
[15] P. Jena, B. K. Rao, and S. N. Khanna, *Physics and Chemistry of Small Clusters* (Plenum, New York, 1987).
[16] I. Prigogine and S. A. Rice, in *Evolution of Size Effect in Chemical Dynamics*, special issue of Adv. Chem. Phys. **70** (Wiley, New York, 1988).
[17] S. Iijima and T. Ichihashi, Phys. Rev. Lett. **56**, 616 (1986).
[18] N. Doraiswamy and L. D. Marks, Philos. Mag. B **71**, 291 (1995).
[19] D. Narayanaswamy and L. D. Marks, Z. Phys. D **26**, S70 (1993).
[20] P. M. Ajayan and I. D. Marks, Phys. Rev. Lett. **17**, 279 (1989).
[21] L. D. Marks, Philos. Mag. A **49**, 81 (1984).
[22] G. Honjo and K. Yagi, J. Vac. Sci. Technol. **6**, 576 (1969).