

MATERIALS SCIENCE

Crystal plane orientation-dependent surface atom diffusion in sub-10-nm Au nanocrystals

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Surface atom diffusion is a ubiquitous phenomenon in nanostructured metals with ultrahigh surface-to-volume ratios. However, the fundamental atomic mechanism of surface atom diffusion remains elusive. Here, we report in situ atomic-scale observations of surface pressure-driven atom diffusion in gold nanocrystals at room temperature using high-resolution transmission electron microscopy with a high-speed detection camera. The topmost layer of atoms on (001) plane initially diffuse in a column-by-column manner. As diffusion proceeds, the remaining atomic columns collectively inject into adjacent underlayer, accompanied by nucleation of a surface dislocation. In comparison, atoms on (111) plane directly diffuse to the base without collective injection. Quantitative calculations indicate that these crystal plane orientation-dependent atom diffusion behaviors contribute to the larger diffusion coefficient of (111) plane compared to (001) plane in addition to the effect of diffusion activation energy. Our findings provide valuable insights into atomic mechanisms of diffusion-dominant morphology evolution of nanostructured metals and guide the design of nanostructured materials with enhanced structural stability.

INTRODUCTION

Nanostructured metals have extensive applications as catalysts, electrodes, interconnects, and more, owing to their multifunctional and structure-dependent properties (1–4). As the characteristic external size decreases to tens of nanometers or sub-10-nm, nanostructured metals generally exhibit optimized performances (5, 6). However, the reduced size and increased surface fraction will undoubtedly promote surface atom diffusion compared to the bulk counterparts and thus lead to remarkable time-dependent morphology evolution and structural instability (7–11). Over recent decades, surface atom diffusion involving the motion of atoms on the surface of a metal material has emerged as an important issue. Taking a typical face-centered cubic (FCC) metal—Au as an example—the surface morphology evolution, the surface diffusion activation energy, and the associated diffusion coefficient have been investigated. The diffusion coefficient at room temperature was reported to vary in a wide range from 10^{-20} to 10^{-14} cm²/s (12–15). However, a more accurate diffusion coefficient has not yet been determined with direct experimental observations.

Moreover, despite several models including single adatom hopping and atom chain diffusion predicted by molecular dynamics simulations (16), surface atom diffusion dynamics has been rarely studied experimentally until now limited by either spatial or temporal resolution. In particular, the atom diffusion behaviors and the corresponding

kinetic parameters on different crystal planes have not been elucidated yet. It has been reported that the topmost atoms diffusing on (001) plane can reconstruct to form surface dislocations (17–22). Also, surface dislocation nucleation is considered to avoid the so-called Ehrlich-Schwoebel energy barrier, i.e., the energy barrier required for individual atoms descending over a step from high to low atomic layers (23–25). However, the impact of surface dislocation on atom diffusion process and diffusion coefficient remains unclear.

Here, combining in situ Cs-corrected transmission electron microscopy (TEM) with a high-speed detection camera, we have successfully captured the instantaneous transition of surface atoms on different crystal planes of Au nanocrystals at atomic scale. Two distinct diffusion manners on (001) and (111) planes were observed. The topmost layer of atoms on (001) plane diffuse to the base, i.e., the nearby flat surface of the Au nanocrystals in a column-by-column manner. Sequentially, several atom columns collectively inject into the adjacent underlayer. In comparison, atoms on (111) plane directly diffuse to the base rapidly merely in form of individual atomic column. Specifically, although surface dislocation nucleation on (001) plane can accelerate instantaneous atom diffusion, quantitative calculations demonstrated that the diffusion coefficient of (111) plane is approximately one order of magnitude higher than that of (001) plane. This discrepancy originated from the differences in diffusion behaviors and diffusion activation energy. Our findings provide insights into crystal plane orientation-dependent surface atom diffusion in nanostructured metals, shedding light on the atomic-scale mechanisms of diffusion-dominant morphology evolution of nanostructured metals.

RESULTS

Layer-by-layer diffusion process

The nanoporous gold (NPG) film with a thickness of ~100 nm was prepared by electrochemical dealloying of Ag from a white gold leaf [Ag₆₅Au₃₅ atomic % (at %)]. With a three-dimensional self-supporting architecture, the NPG film contains abundant Au ligaments (fig. S1A). The size of the ligaments, comparable to that of the nanopores, falls in a wide distribution range from ~2 to 35 nm with an average size

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of ~ 20 nm (26). In situ TEM tensile tests were conducted by a home-made strain actuator (fig. S1B) (27–30). Under tensile straining, the Au ligaments underwent severe deformation and fracture. Figure 1A shows a high-resolution TEM (HRTEM) image of a ligament with a diameter of 1 nm just before fracture. The crystallographic orientation of the ligament is along $[110]$ direction. The applied tensile load σ along $\langle 112 \rangle$ direction is indicated by the white double-headed arrows. As depicted in Fig. 1B, once the ligament fractured, the atoms on the upper surface migrated rapidly, resulting in a hill-like structure with a blunt surface. Subsequently, the uppermost atoms continued to move toward the base, i.e., the nearby flat surface on both sides of the hill-like structure of the crystal, thereby leading to remarkable morphology evolution, as shown in Fig. 1 (B to E). Specifically, using the base plane marked by the white dashed line as a reference point, the (001) planes were numbered from “1” to “9,” starting from the top of the hill-like structure to facilitate the tracking of atom diffusion process. Notably, the topmost atoms diffused layer by layer and the inner pristine atomic planes were gradually exposed, leading to a more pronounced blunting surface with a larger curvature radius as indicated by the yellow dashed arcs. A detailed illustration of this dynamic process is shown in movie S1. The morphology evolution of the hill-like structure can be aptly described as a liquid drop-like behavior (9, 11, 16). Massive surface atom diffused from the hill-like structure’s dome toward its base is driven by the surface pressure (i.e., capillary forces) originating from both curvature and surface energy effects (fig. S2). The initial surface pressure of the topmost layer of the hill-like structure was calculated to reach as high as 1.91 GPa indicated in fig. S2C, which was sufficiently high to break the Au atomic bonds, thus driving surface atom diffusion. As diffusion proceeded, the curvature radius of the hill-like structure increased, leading to a gradual reduction in surface pressure.

Consequently, atom diffusion progressively decelerated and eventually stopped.

Surface atom diffusion on (001) plane

To investigate the diffusion dynamics in detail, the atom diffusion behaviors on layers “5” and “6” were analyzed as illustrative examples. Figure 2 presents a time series of HRTEM images showing the evolution of the atomic column configurations on the topmost layers with the schematic illustrations presented in the insets. As shown in Fig. 2 (A to E), the number of the atomic columns on the topmost (001) plane, i.e., layer 5 indicated by the red arrows, progressively decreased from 9 to 4 one by one. In other words, the atomic columns at the margins diffused individually to the base. In Fig. 2 (E and F), four atomic columns on layer 5 collectively injected into layer 6. As indicated by the red triangle, these atoms were reconstructed, forming an extra row of atomic column on layer 6, determined as a two-dimensional defect, namely, surface dislocation. Following a pattern akin to the diffusion behaviors on layer 5, the atomic columns on layer 6 initially diffused one after the other, resulting in a sequential decrease in their number from 10 to 5, as shown in Fig. 2 (F to I). Subsequently, the remaining five atomic columns collectively injected into layer “7” accompanied by the formation of a surface dislocation, as indicated by the red triangle in Fig. 2J. In addition, this diffusion behavior was further manifested on layer 7, as shown in fig. S3. Thus, it can be concluded that surface atoms diffusion on (001) plane can transfer in two different manners including diffusion by individual atomic column and collective injection by several atomic columns into the adjacent underlayer with a surface dislocation nucleation. At the initial diffusion stage, atoms tend to diffuse in the first manner, while as the number of atomic columns decreases to four or five, atomic columns collectively inject into the adjacent underlayer

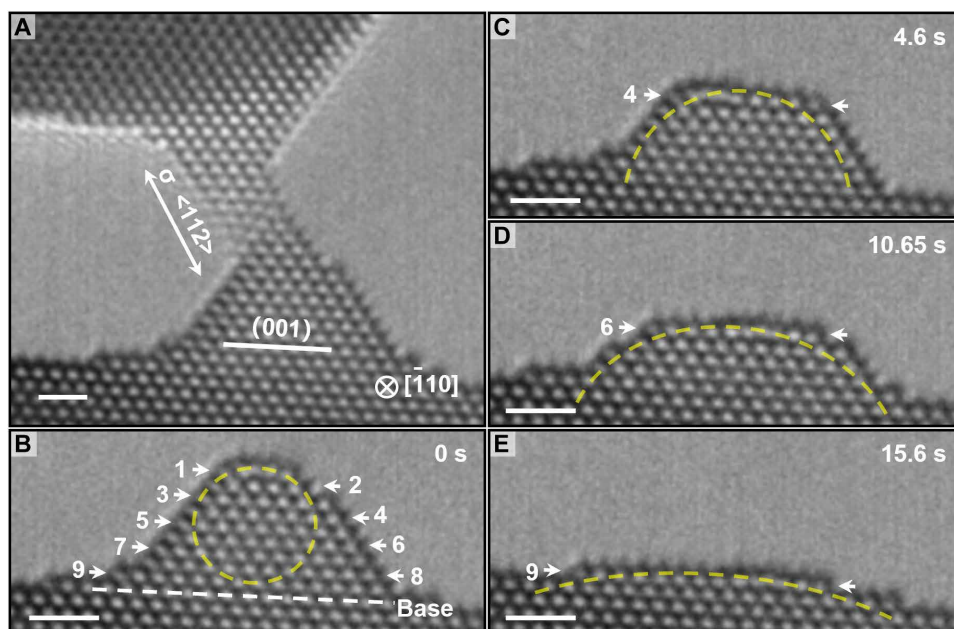


Fig. 1. HRTEM images of surface atoms layer-by-layer diffusion process of fractured Au ligament. (A) Fourier-filtered HRTEM image of an Au ligament. The applied tensile stress σ is denoted by the white double-headed arrow. The bright dots represent Au atomic columns along the view direction, i.e., $[110]$ direction. (B to E) Successive Fourier-filtered HRTEM images showing the layer-by-layer retreat of (001) atomic plane. The yellow dashed arcs indicate the curvature radius of the hill-like structure. Scale bars, 1 nm.

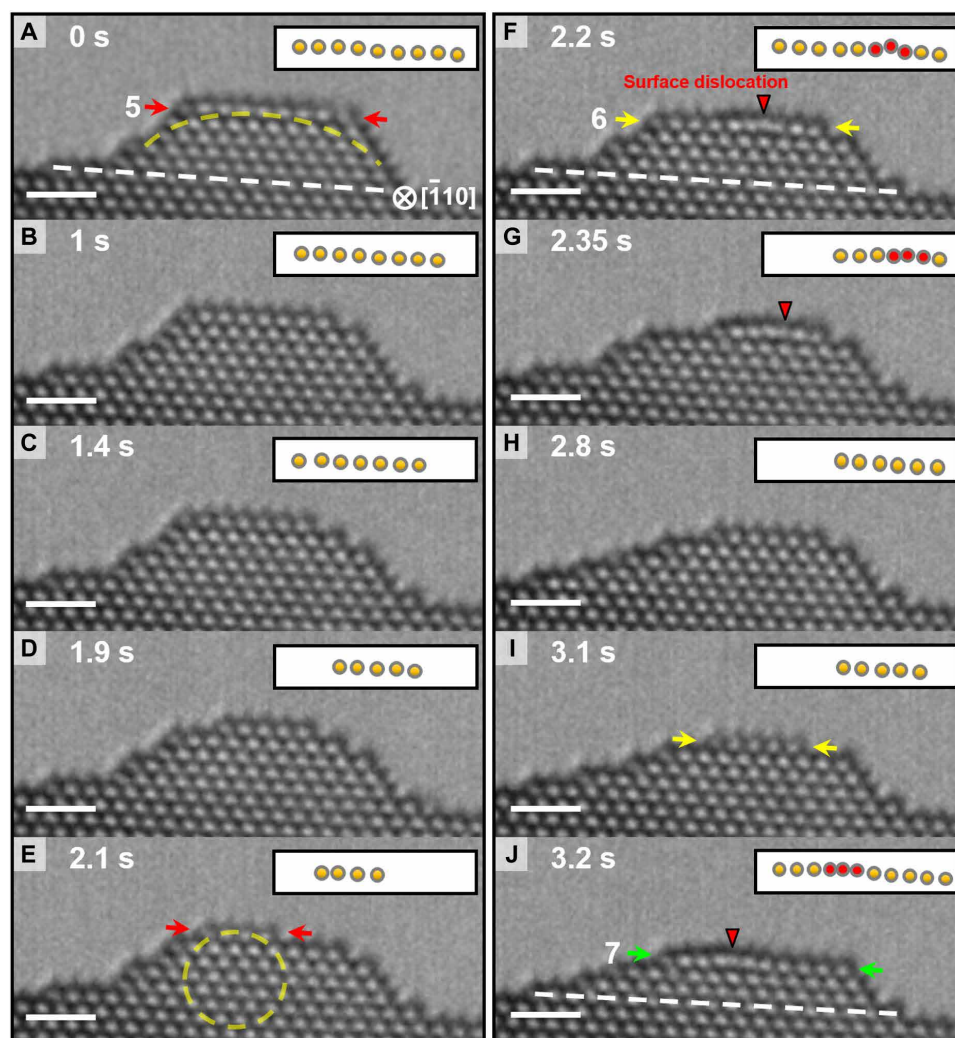


Fig. 2. HRTEM images of surface atom diffusion on (001) plane. (A to J) A time series of Fourier-filtered HRTEM images showing the surface atom diffusion process on layers 5 and 6. The surface dislocation core is denoted by the red triangles. The insets on the top right represent the schematic illustrations of the atom configurations on the topmost layer. Yellow dashed arcs indicate the local curvature radius of the topmost atomic layer. Scale bars, 1 nm.

in the second manner. The change in diffusion mode is deduced to be related to the local driving force of atomic diffusion, i.e., the curvature radius of the topmost atomic layer. Taking layer 5 for example, the relationship between the curvature of the topmost atomic layer and atomic column diffusion velocity was analyzed. As plotted in fig. S4B, the atomic diffusion rate ($1/t$) is a linear function of the curvature of the topmost atomic layer. As the diffusion proceeds, the number of atomic columns decreases and the local curvature of the atomic layer increases, leading to a corresponding augmentation in the surface pressure and velocity of atomic diffusion. This result implies that surface atomic diffusion is directly influenced by the surface pressure originating from curvature and surface energy effect. Thus, the transition of the diffusion mode can be attributed to the reduction in the local curvature radius of the topmost atomic layer and the simultaneous increase of the driving force for atom diffusion, as illustrated by the yellow dashed arcs in Fig. 2 (A to E).

During the column-by-column diffusion of atoms, removal and adding back of atomic columns were also observed, as indicated by

purple triangle in fig. S5 (F to H) and by cyan triangle in fig. S6. It is deduced that after the atoms on the edge diffused downward, the remaining atoms on the top surface underwent structural relaxation to the side sites. This may be related to the local equilibrium of vacancy-atom configurations or to the atomic diffusion kinetics involving diffusion distances and energy barriers. In addition, it was found that the crystal plane orientation of the side facets dynamically changes with the collapse of the hill-like structure, as shown in fig. S7. The left and right facets changed from the initial $(\bar{1}\bar{1}1)$ plane to the $(\bar{1}\bar{1}7)$ plane and from (111) plane to the (113) plane, respectively. This is mainly caused by the diffusion of a few atoms from the top surface to the side planes (indicated by blue arrows in fig. S7, C to E) and the gradual collapse of the hill-like structure. That is to say, the dynamic morphology evolution of the hill-like structure can be primarily attributed to the sequential layer-by-layer downward diffusion of atoms from the topmost layer, rather than substantial atom diffusion on the side planes. It is worth noting that previous reports have suggested that the crystal plane orientation of side facets may influence the energy

barrier for the downward diffusion of topmost atoms (31). However, the resultant influence on diffusion behaviors and the morphology evolution are not yet clear and can be investigated in the future.

Nucleation of surface dislocation on (001) plane

Although surface dislocations nucleation from several atomic columns reconstruction on (001) plane has been previously reported (17–22), the detailed process of nucleation and the role of surface dislocation in atom diffusion remain incomprehensively elucidated. In Fig. 3 (A to D), we present a time series of HRTEM images with an extremely high frame rate of 0.01 s, depicting the nucleation and motion of a surface dislocation on layer 7. From 0.00 to 0.01 s, the upper five atomic columns on layer 6 were collectively injected into layer 7, resulting in a more compact and disordered arrangement of atomic columns near the injection area on layer 7. At 0.02 s, the number of atomic columns on layer 7 is increased undeniably by one column, as indicated by red arrow points, implying the rearrangement of atomic columns and the formation of a surface dislocation. To elucidate the atom diffusion path and the positions of atomic columns

more explicitly than through visual inspection, we used an automated atomic column tracking method based on previous studies (32). This method can automatically label atomic columns and thus can correlate them between successive images during surface atom diffusion. The atomic columns injection process with the nucleation of a surface dislocation was substantiated by the automated atomic column tracking method as shown by an atomic column displacement map of Fig. 3E. Atomic columns at different times are represented by circles of varying sizes and colors. The upper right image is an enlarged view within the dotted box. Each short black arrow represents the displacement vector of an atomic column between successive images, with the length denoting the magnitude of the displacement. From 0.00 to 0.02 s, the emergence of a new atomic column was observed on layer 7, indicated by a green arrow originating from the injection of five atomic columns. Moreover, we observed that the two atomic columns adjacent to the new column shifted to the left and right, respectively, exhibiting more displacement than the other columns to better accommodate the insertion of the new atomic column. Although the adjacent atomic columns were adjusted, the atoms at the

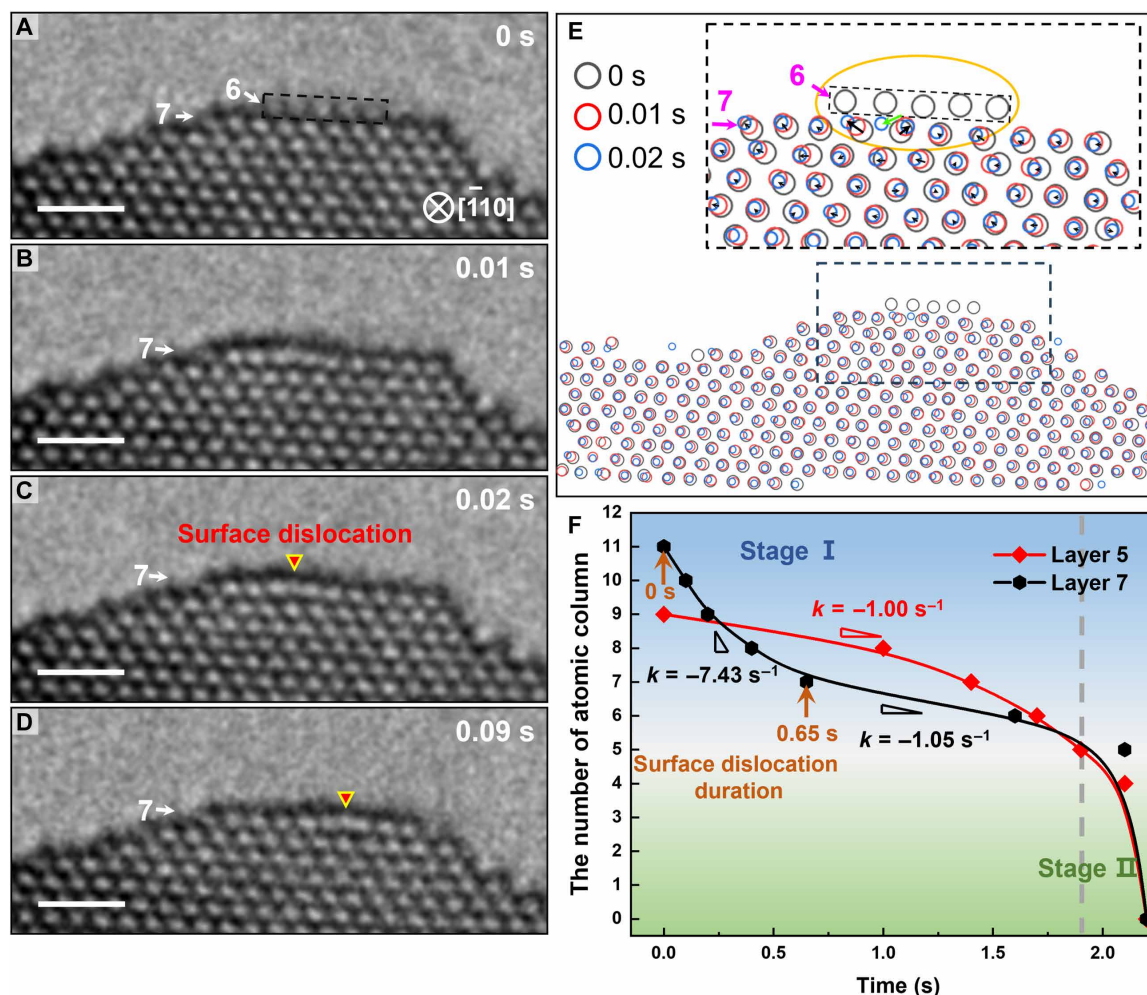


Fig. 3. HRTEM images and computational simulation showing the nucleation of surface dislocation. (A to D) A time series of Fourier-filtered HRTEM images showing the nucleation and movement of a surface dislocation. Scale bars: 1 nm. (E) Atomic column trajectories and associated atomic displacement map extracted from (A) to (C) from automated analysis. The upper right image is an enlarged image in the dotted box. (F) The number of atomic columns on layers 5 and 7 is plotted as a function of time. Brown arrows indicate surface dislocation duration on layer 7.

surface dislocation core are more tightly packed than elsewhere, implying the induction of local drastic compressive strain by the surface dislocation confirmed by fig. S8. As shown in Fig. 3 (C and D) and the corresponding atomic displacement map extracted from Fig. 3 (C and D) in fig. S9, the surface dislocation, marked by the red arrow, moved rapidly on layer 7. This led to a consequent fluctuation of the compressive strain filed at the dislocation core. Thus, this process could promote the instability of the atomic arrangement and facilitate fast atom diffusion at the topmost layer. As individual atomic column diffused downward, the atomic column reconstruction and the surface dislocation nucleation could be driven by the reduced local curvature radius and thus an increased surface pressure. Despite the introduction of extra local strain energy, surface dislocation is considered to be spontaneously nucleated due to a negative formation energy (18). Furthermore, the collective injection of several atomic columns into the lower layer accompanied by dislocation nucleation circumvents the Ehrlich-Schwoebel barrier (17).

To investigate the role of surface dislocations on atomic diffusion, we perform a quantitative analysis of the number of atomic columns on layer 5 and layer 7 over time, as shown in Fig. 3F. For comparison, the atom diffusion on layer 5 did not involve any surface dislocation, while atom diffusion on layer 7 was accompanied by a surface dislocation. The slope of the curve represents the rate at which the number of atomic columns decreased, i.e., the rate of atom diffusion. A larger slope indicates a faster rate of atom diffusion. At stage I, when atomic columns diffused individually column by column, the curve of layer 7 exhibits a much larger slope of -7.43 s^{-1} than the curve of layer 5 with a slope of -1.00 s^{-1} before $t = 0.65 \text{ s}$. This indicates that the formation of surface dislocation notably accelerated the surface atom diffusion on layer 7. However, such a contribution of speeding up atom diffusion is short-lived and instantaneous, as the surface dislocation annihilated at $t = 0.65 \text{ s}$ in fig. S3 (E and F). Consequently, the slope of the curve of layer 7 decreased to -1.05 s^{-1} , reaching a similar level to that of layer 5. In addition, we clarified that surface dislocations are annihilated through the merging of two adjacent atomic columns at the dislocation core, as illustrated in fig. S10. In essence, because of the limited duration of the surface dislocation, the effect of enhancing atom diffusion only works for a short time during stage I. At the later diffusion stage (stage II), the atoms on both layers 5 and 7 fleetly diffused into the adjacent underlayer in a collective injection manner. The curves of both layers 5 and 7 show similar large slopes.

Surface atom diffusion on (111) plane

In addition, the surface atom diffusion on (111) plane was analyzed to investigate the effect of crystal plane orientations on surface atom diffusion. Figure 4 (A to I) presents a time series of HRTEM images showing the morphology evolution of another Au ligament. Similar to the diffusion process observed on (001) plane, once the hill-like structure was formed after fracture, the topmost atoms on (111) plane was diffused layer by layer. In Fig. 4 (B to E), the upper atomic layers (layers 1 to “3”) rapidly diffused and disappeared, with detailed surface atom diffusion behaviors not captured. Atom diffusion behaviors on layer “4” are presented in Fig. 4 (E to I). Initially, the topmost atomic columns steadily diffused individually to the base, and the number of atomic columns decreased from 10 to 5. Then, the remaining atomic columns became less stable and diffused at a faster rate. Notably, the number of atomic columns on layer 5 did not increase after the complete atom diffusion of layer 4. That is to

say, all the atomic columns on layer 4 diffused directly to the base without any collective injection into the adjacent underlayer. Also, it is worth noting that no surface dislocation nucleation on layer 5 was found, which is essentially different from the surface dislocation-mediated diffusion process on (001) plane. We attribute this to the (111) plane being a close-packed plane of FCC structure. In contrast to (001) plane, the atomic arrangement on (111) plane is more compact and stable, rendering the atomic columns rearrangement process less likely to occur. Consequently, surface atoms on (111) plane do not inject into the adjacent underlayer to rearrange and form a surface dislocation. Instead, they diffuse directly to the base. Figure 4 (J and K) shows the schematic illustrations of atom diffusion on (001, 111) planes, respectively. It can be found that the diffusion process of (001) plane can be divided into two manners as aforementioned. First, the topmost atomic column steadily diffused to the base in the form of individual atomic column. Afterward, the remaining four or five atomic columns collectively inject into the adjacent underlayer accompanied by the nucleation of a surface dislocation. For the atom diffusion on (111) plane, the atomic columns directly diffuse to the base without any collective injection process.

Surface atom diffusion coefficient calculation

To facilitate an accurate comparison of atomic diffusion kinetic parameters on different crystal planes, we quantitatively calculated the surface atom diffusion coefficients. On the basis of the morphology evolution of the hill-like structure, the surface atom diffusion coefficient related to mobility by Einstein relation can be expressed as (33)

$$J_s = -\frac{X_s}{\Omega} \delta_s \frac{D_s}{k_B T} \partial_s \mu \quad (1)$$

where J_s is the mass flux of surface atom, X_s is the solubility of diffusing atom in surface liquid layer (~ 1), Ω is the atomic volume (for Au, $\Omega = 0.01248 \text{ nm}^3$ per atom), δ_s is the nominal surface layer thickness (for the uppermost atomic layer, $\delta_s \sim 0.2$ to 0.3 nm), D_s is surface atom diffusion coefficient, k_B is the Boltzmann constant, T is kelvin temperature (here $T = 320 \text{ K}$), μ is chemical potential at different positions of the structure ($\mu = \frac{\gamma R}{2}$), γ is the surface energy, and R is the curvature radius. Meanwhile, mass conservation is required, given by $\partial_t h + \Omega \partial_s J_s = 0$, where h is the height of the hill-like structure. Thus, the surface diffusion coefficient can be calculated according to the following equation (10)

$$D_s = \frac{h}{\Delta t} R^3 \frac{k_B T}{X_s \delta_s \gamma \Omega} \quad (2)$$

where Δt is the time for structure evolution. The calculated D_s of atom diffusion on (001) and (111) planes are 1.75×10^{-15} and $1.63 \times 10^{-14} \text{ cm}^2/\text{s}$, respectively. This implies that the diffusion coefficient on (111) plane is one order of magnitude higher than that on (001) plane. Given the proximity of the initial curvature radius for the two hill-like structures [0.91 and 1.09 nm for (001) and (111) plane, respectively], the effect of the initial curvature radius can be neglected. Thus, the discrepancy of the diffusion coefficients on different planes primarily arises from the surface energy γ [$\gamma_{(001)} = 0.864 \text{ J/m}^2$ and $\gamma_{(111)} = 0.704 \text{ J/m}^2$] as well as $\frac{h}{\Delta t}$ (34), which can be calculated from the slopes of the curves shown in Fig. 5. It is apparent that the parameter $\frac{h}{\Delta t}$ is a macroscopic manifestation of the atom diffusion behaviors. To be specific, atoms on (111) plane consistently diffuse toward the base directly, while on (001) plane, atoms can diffuse to the adjacent underlayer by collective injection, which will slow

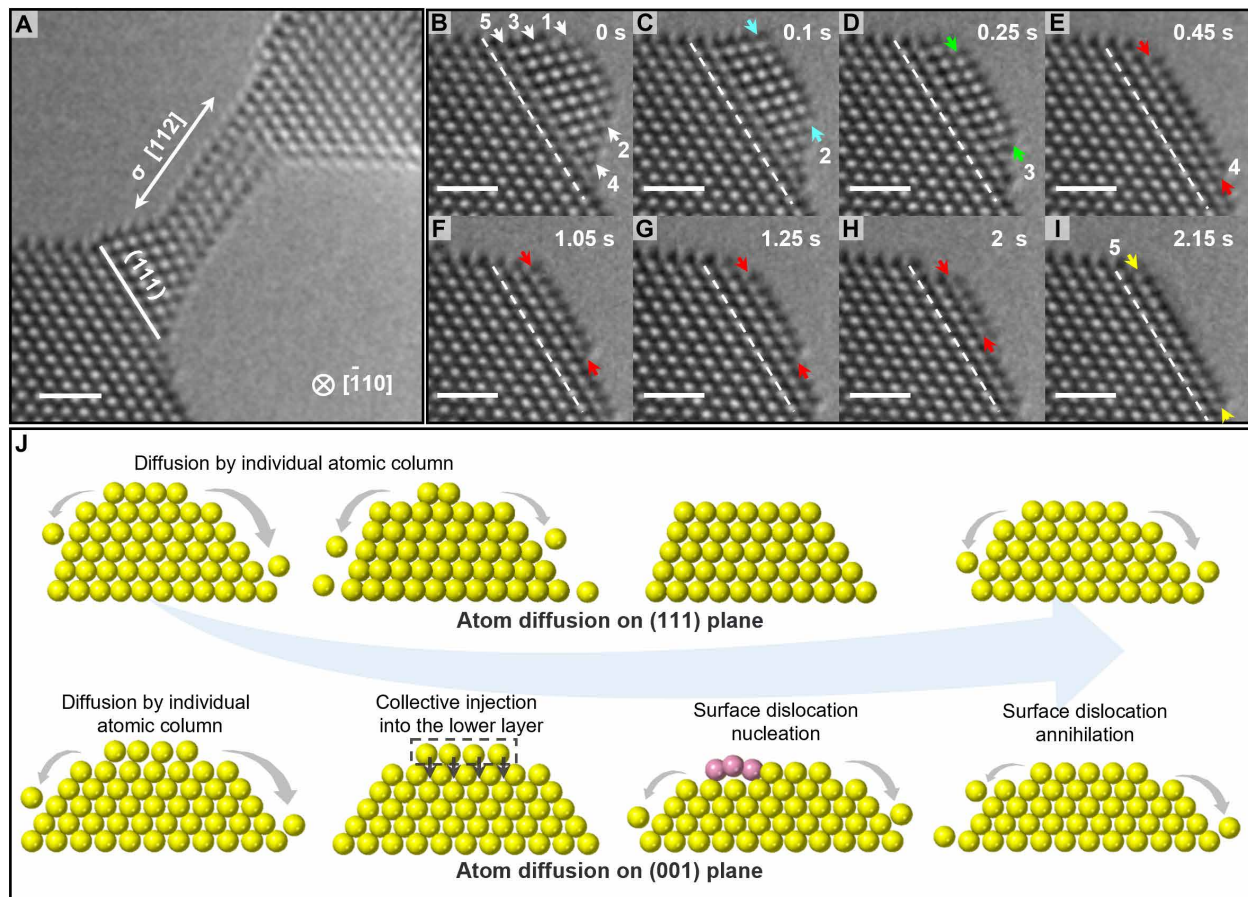


Fig. 4. HRTEM images of surface atom diffusion on (111) plane. (A) Fourier-filtered HRTEM image of an Au nanowire. The applied tensile stress σ is denoted by the white double-headed arrow. (B to I) Successive Fourier-filtered HRTEM images showing layer-by-layer diffusion on (111) plane. Scale bars: 1 nm. (J) A schematic illustration of the monolayer atom diffusion process of (111) and (001) plane. The yellow and pink spheres represent the Au atoms and the surface dislocation core, respectively.

down the height h reduction and lead to a smaller diffusion coefficient. In addition, although surface dislocations can enhance the instability of atom configurations and boost instantaneous atom diffusion, their short survival duration limits their notable contribution to the overall diffusion coefficient.

The diffusion coefficients on (001) plane and (111) plane were further calculated and compared based on the empirical Arrhenius formula (35)

$$D_s = D_0 \exp\left(-\frac{E_a}{k_B T}\right) \quad (3)$$

where D_0 is the pre-exponential factor, E_a is the activation energy, and k_B is the Boltzmann constant. For atom diffusion on (001) plane, $D_{0(001)} = 8.0 \times 10^{-4}$ to 1.0×10^{-2} cm²/s (35) and $E_{a(001)} = 0.84$ eV (36). For diffusion on (111) plane, $D_{0(111)} = 2 \times 10^{-4}$ to 3.7×10^{-4} cm²/s (35) and $E_{a(111)} = 0.67$ eV (37, 38). At $T = 320$ K, the diffusion coefficients D_s on (001) and (111) planes are determined to be 4.92×10^{-17} to 6.15×10^{-16} cm²/s and 5.79×10^{-15} to 1.07×10^{-14} cm²/s, respectively. This analysis further confirms the crystal plane dependence of the diffusion coefficient, i.e., the atom diffusion coefficient on (111) plane is larger than that on (001) plane.

To further analyze the intrinsic flow characteristic of the Au nanocrystal, the viscosity, an important kinetic parameter was calculated.

As previously reported, the liquid drop-like morphology evolution of the Au nanocrystal can be defined as “Coble pseudoelasticity” (10, 16). The strain rate of Coble creep can be expressed by the following equation (39)

$$\dot{\epsilon} = A_c \frac{\delta_s D_s \Omega}{d^3 k_B T} \sigma \quad (4)$$

where $\dot{\epsilon}$ is the strain rate, A_c is the dimensionless constant (30 to 50), δ_s is the nominal surface layer thickness (for the topmost atomic layer, $\delta_s \sim 0.2$ to 0.3 nm), D_s is the surface atoms diffusivity, Ω is the atomic volume, d is the initial diameter of the hill-like structure, k_B is the Boltzmann constant, T is the kelvin temperature (here $T = 320$ K), and σ is the surface pressure. By combining Eq. 3 with the classic viscosity equation, $\eta = \frac{\sigma}{\dot{\epsilon}}$, the viscosity can be deduced by the following equation

$$\eta = \frac{d^3 k_B T}{A_c \delta_s D_s \Omega} \quad (5)$$

The calculated D_s on (001) and (111) planes based on Eq. 2 are 1.75×10^{-15} and 1.63×10^{-14} cm²/s, respectively. Thus, the surface viscosities of (001) and (111) planes are determined to be 1.35×10^9 and 2.50×10^8 Pa·s, respectively. These values closely resemble those of metallic glassy nanoparticle’s viscosities (40). According to Eq. 4, the

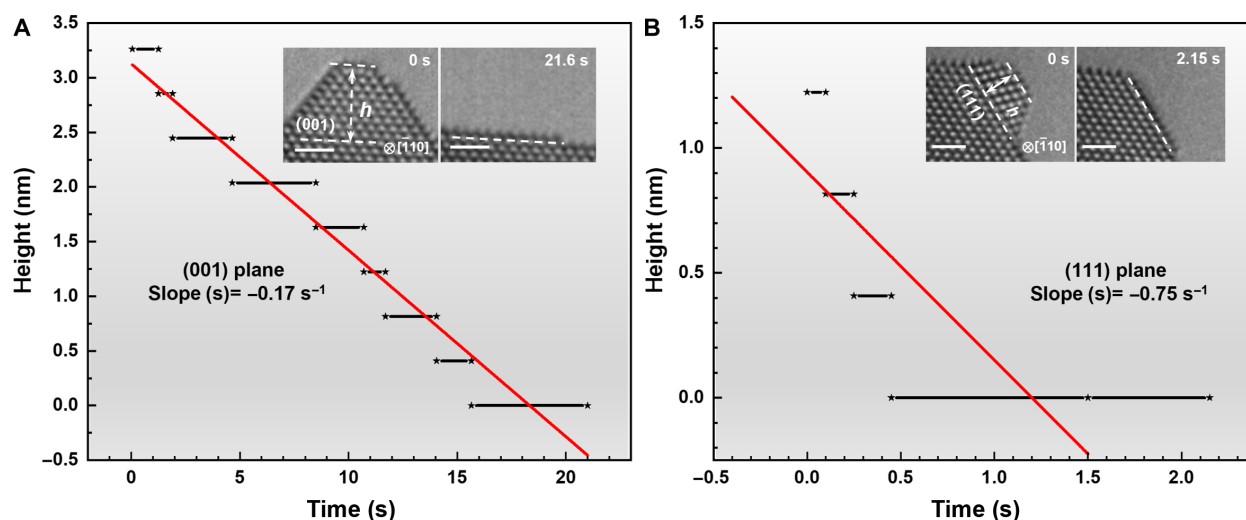


Fig. 5. Diffusion coefficient calculation. (A to B) Measured retreating distance h of (001) and (111) atomic planes versus time. The slopes of the fitted lines are -0.17 (A) and -0.75 s^{-1} (B), respectively. The morphology evolutions of the fractured Au hill-like structures are shown on the top right. Scale bars, 1 nm.

viscosity is correlated with the diffusion coefficient, implying that the viscosity is also orientation dependent. In contrast to previous studies that qualitatively defined the liquid drop-like behaviors based on the morphology evolution (9, 11, 16), we provide a quantitative description of the diffusion-dominated flow characteristic of Au nanocrystals.

DISCUSSION

In this study, surface atom diffusion behaviors correlated with crystal plane orientation in sub-10-nm Au nanocrystals were directly uncovered. The diffusion kinetic parameters on different crystal plane orientations were further calculated quantitatively. Here, the diffusion-mediated morphology evolution is completely spontaneous and driven by intrinsic surface pressure with no external load. Moreover, this morphology evolution is a pure diffusion process that does not involve any dislocation slip, which is completely different from the diffusion-assisted deformation behaviors reported by Zhong *et al.* (41) and Sun *et al.* (42). Although the liquid drop-like morphology evolution of Ag nanocrystals has been reported by Sun *et al.* (16), the atom diffusion behaviors were predicted by molecular dynamics simulation. In contrast, our work provides direct and reliable experimental results with temporal and atomic resolution for understanding intrinsic physics of pure diffusion-mediated deformation associated with Coble creep in metal nanocrystals.

Further analysis shows that this liquid drop-like morphology evolution due to layer-by-layer atom diffusion is actually independent of the initial curvature. As shown in figs. S11, S12, and S13, the morphology evolution of hill-like structures with three different initial curvatures is dominated by layer-by-layer diffusion of the topmost atoms, and the diffusion kinetic parameters are also similar. In addition, the heating and atom knock-on effects introduced by the electron beam on the sample are further discussed. As reported in our previous work (27), the maximum increase of temperature in Au nanocrystals induced by electron beam was estimated to be $\sim 3.8 \text{ K}$, which has a minimal effect on promoting atom diffusion. The maximum energy that an electron beam can transfer to the Au atom is $\sim 2.66 \text{ eV}$ when the TEM is operated at 200 kV, which is much lower than the threshold displacement energy (i.e., a minimum

amount of kinetic energy transferred to a lattice atom that results in the formation of a point defect) of $\sim 36 \text{ eV}$ for Au (43). Hence, the knock-on displacement of electron beam on Au atoms is also negligible. In our previous study (26), a 2.5-nm-wide Au nanocrystal with atomic-level surface steps was subjected to electron beam irradiation (electron dose of $\sim 2500 \text{ electrons/nm}^2$) for 15 and 30 min, respectively, and no obvious structure change was observed.

In this work, atom diffusion behaviors of sub-10-nm Au nanocrystals were investigated in detail at atomic scale. Although atom diffusion on both (001) and (111) planes resulted in liquid drop-like behaviors, according to direct observations with an ultrahigh frame rate, the migration paths of the surface atoms are essentially different. The crystal plane orientation-dependent diffusion behaviors directly contribute to the apparent discrepancy of the diffusion coefficients on (001) and (111) planes as quantitatively calculated. Moreover, the viscosities were calculated for (001) and (111) planes, respectively, to describe the flow characteristic of Au nanocrystals. Our findings offer a profound understanding of the atomic-scale morphology evolution in nanostructured metals, offering valuable guidance for material structural design.

MATERIALS AND METHODS

In situ TEM straining experiment

In situ straining test was carried out using a double-tilt straining holder (Bestron Science and Technology Co., LTD, Beijing). A miniature device was fixed on this custom-designed TEM sample holder to apply force and displacement by a strain actuator. The holder enables controllable tension deformation of the sample and a range of $\pm 25^\circ$ x -tilt and $\pm 25^\circ$ y -tilt (27–30). The NPG sample was subjected to a strain rate of $\sim 10^{-3} \text{ s}^{-1}$ by controlling the actuator. Meanwhile, the NPG sample was tilted to the desired crystallographic zone axis for atomic-scale observation.

Trajectory tracking by atom column detection and cross-correlation between frames

To identify the positions of atomic columns, we initially normalize the pixel intensity matrix I as follows: $A_w^t = (I - I_{\min}) / (I_{\max} - I_{\min})$.

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