Distance Control of Electromigration-Induced Silver Nanogaps

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Electromigration (EM) in Ag nanocontacts (NCs) was observed in situ on an atomic scale using simultaneous measurements of electrical conductance and mechanical stress. The in situ observations showed that the critical bias voltage of EM was 45 mV. As the bias voltage was increased to 100–200 mV, the NCs broke and gaps with distances of \(1.3 \pm 0.8\) nm were obtained for NCs having widths smaller than 6 nm. When the bias voltage was further increased to 200–300 mV, the gaps expanded to more than 3 nm, regardless of the NC width. It was found that the nanogap distance could be controlled to fit specific molecular sizes by appropriately selecting the bias voltage and NC width.

Keywords: Nanospace, Nanogap, Silver, Electromigration, Nanocontact.

1. INTRODUCTION

Nanospaces have great potential for use in nanoarchitectonics, advanced electronics, and macroscopic applications. Various types of confined nanospaces, such as carbon nanocages, have been developed, as the relentless miniaturization of electronic devices and structural materials continues to progress. Further, open nanospaces have been produced using two metallic electrodes separated by distances of less than several nanometers. Such metallic nanogaps have been used to sandwich single molecules, resulting in the formation of single-molecule junctions (SMJs). To fabricate SMJs, two metal electrodes should be accurately separated to the size of individual molecules. However, the resolutions of present lithographic techniques are at most a few tens of nanometers. To obtain narrower nanogaps, nanocontacts (NCs) have been fractured using electromigration (EM). The analysis of EM processes facilitates the development of nanogap control. In situ high-resolution transmission electron microscopy (HRTEM) enables us to observe the atomic process of EM. In this paper, we demonstrate formation of silver (Ag) nanogaps using EM and control of nanogap distances.

2. EXPERIMENTAL METHODS

We used in situ HRTEM combined with subnanonewton force measurements, which are used in atomic force microscopy (AFM), and electrical conductance measurements, which are used in scanning tunneling microscopy. We prepared two types of Ag nanotips. As one type, Ag was evaporated in a vacuum chamber and deposited on a nanotip attached on a Si cantilever for AFM. As another type, a rectangular Ag plate was prepared and its contact edge was thinned by argon ion milling, followed by the formation of Ag tips of 2–9 nm width and 5–20 nm thickness. Inside the transmission electron microscope at the University of Tsukuba for in situ nanotip manipulation (JEOL JEM-2011KZ), the cantilever tip was brought into contact with the edge surface of the opposing plate using piezodriving. The cantilever tip was pressed into the plate edge to prepare NCs and then retracted to thin them. After the tip was fixed, a bias voltage was applied to cause EM. These manipulations were performed at room temperature. Structural dynamics during the process were observed in situ by HRTEM lattice imaging using a television capture system (Gatan 622SC). The time resolution of image observations was 17 ms. The force acting on the contacts was simultaneously measured by optical detection of cantilever deflection. The electrical conductance was measured using a two-terminal method. The results of high-resolution...
imaging and signal detection in this system were simultaneously recorded and analyzed for every image.

3. RESULTS

Figure 1 shows the time sequence of high-resolution images of structural variation in a Ag NC during EM while applying a bias voltage of 0–100 mV. The cantilever tip in the upper region of each frame in Figure 1 was positively biased and the plate in the lower region was negatively biased. The NC lies between the cantilever tip and the plate. Neither contamination nor an oxide layer was observed on the surfaces of either the tip or plate, as shown in Figures 1(a)–(f). The (111) lattice fringes with a 0.24 nm spacing were observed both on the tip and the plate. As the bias voltage was increased up to 45 mV, no change in the external shape of the NC was observed (Fig. 1(a)). This critical voltage is smaller than those for Au and Cu NCs (80 mV and 240 mV, respectively).

Above 45 mV, quick repetition of the expansion and shrinkage of the most constricted region was observed, indicating that EM started at this voltage. Subsequently, above this critical voltage the NC thinned during the repetition (Fig. 1(b)). The minimum width of the NC decreased from 2.4 to 1.9, 1.7, 1.2, and 0.3 nm with increasing voltage (Figs. 1(a)–(e)). The narrowest width, i.e., 0.3 nm, corresponds to a single-atom width (Fig. 1(e)). Finally, the NC broke and a gap of 1.8 nm was produced (Fig. 1(f)). Note that thinning of the NC proceeded by migration of atoms from the negatively biased side to the positively biased side, and fracture occurred by the dissipation of atoms in the most constricted region.

Figure 2 shows variations in the bias voltage, current, conductance, minimum cross-sectional area, current density, force, and stress of the NC presented in Figure 1 as a function of time. The recording times of the images in Figures 1(a)–(f) are indicated by the labels a–f in Figure 2 (hereafter times a–f in Figs. 1 and 2). We assumed that the minimum cross section of the NC was circular and estimated the area using the minimum cross-sectional width from high-resolution images. The current increased in proportion to the bias voltage. When the bias voltage exceeded the critical value of EM (45 mV), the current fluctuated, as indicated by the arrow in Figure 2. In this process, the minimum cross-sectional area fluctuated by approximately 0.9 nm² in response to the current fluctuation. The conductance first decreased continuously, and then stepwise. The variation in the area was similar to that in the conductance. The current density first increased with the bias voltage. The value of the current density during EM was larger than 10 TA/m². After the bias voltage reached 100 mV, the current density decreased with the decreasing minimum cross-sectional area. A tensile force of 1 nN was first applied at time a to support the NC between the tip and the plate. The force acting on the NC rapidly decreased and became negative at 45 mV, as indicated by the arrow in Figure 2. The negative forces implies that compressive forces were applied to the NC; the NC expanded owing to EM. The force reached −20 nN and then increased. Before fracture, the force changed from negative to positive. Thus, compressive forces acted on the NC during EM. We calculated the stress of the NC by dividing the force by the minimum cross-sectional area. The stress reached approximately −2.4 GPa (compressive stress) during EM and changed to positive before fracture, similar to the variation in the force. After the change, the stress increased to 15 GPa, which exceeds the strength of Ag NCs.

When the NCs did not break, we increased the bias voltage up to 300 mV. Figure 3 shows the time sequence of high-resolution images of structural variation in a Ag NC during EM while applying a bias voltage of 0–300 mV. The initial width of the NC was 6.6 nm (Fig. 3(a)). When
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Figure 2. Variations in bias voltage, current, conductance, minimum cross-sectional area, current density, force, and stress of the Ag NC presented in Figure 1 as function of time. Times indicated by the labels (a)–(f) correspond to those in Figures 1(a)–(f). The crosses indicate fracture. Positive and negative forces correspond to tensile and compressive forces acting on the contact, respectively. The arrow in the current frame indicates the starting point of EM.

the bias voltage reached the critical value, thinning of the NC started. The minimum width of the NC decreased to 4.3 nm at 160 mV (Fig. 3(b)). After the bias voltage reached 300 mV, the fluctuation frequency of the NC exceeded the sampling rate of the observation system (30 Hz), as a result of which the TEM image blurred (Fig. 3(c)). Finally, the NC broke and a nanogap of 9.4 nm was produced (Fig. 3(d)).

Figure 4 shows variations in the bias voltage, current, force, and minimum cross-sectional area for the NC presented in Figure 3 as a function of time. The recording times of the images in Figures 3(a)–(d) are indicated by labels a–d in Figure 4 (hereafter times a–d in Figs. 3 and 4). Similar to the case in Figure 2, the current fluctuated above the critical voltage. Until 300 mV, the fluctuation of the minimum cross-sectional area was approximately 1.5 nm². The current increased as the bias voltage was increased to 300 mV, and then decreased rapidly. The current fluctuation further increased after this rapid decrease. From the critical bias voltage to 300 mV, fluctuations in the minimum cross-sectional area increased to approximately 9 nm² in response to the current fluctuations. The force acting on the NC showed similar variations. The force increased with the bias voltage and fluctuated above the critical voltage. At 300 mV, the force decreased rapidly and the fluctuation amplitude further increased (the force curve gives the appearance of a belt). Notice that the observed forces were positive even after EM occurred, which differs from the case in Figures 1 and 2.

Figure 5 shows high-resolution images of typical Ag nanogaps. The gap distances were 0.5 nm (Fig. 5(a)), 2.0 nm (Fig. 5(b)), and 10.7 nm (Fig. 5(c)). The bias voltages at nanogap formation were 190 mV (Fig. 5(a)), 100 mV (Fig. 5(b)), and 280 mV (Fig. 5(c)).

Figure 6 shows the relationship between gap distance and bias voltage at the fracture of Ag NCs. For bias voltages lower than 100 mV, no gap was formed although EM occurred. At fracture voltages of 100–200 mV, the gap distance was similar, i.e., 1.3 ± 0.8 nm. For higher fracture voltages, the gap distance ranged from 3 to 13 nm.
Figure 4. Variations in bias voltage, current, force, and minimum cross-sectional area of the Ag NC presented in Figure 3 as function of time. Times indicated by arrows (a)–(d) correspond to those of Figures 3(a)–(d). EM starts at 45 mV (time (a)). At 300 mV, large fluctuations in the current and force were observed.

We plotted the observed gap distances against the initial width of Ag NCs before EM, as shown in Figure 7. When the fracture voltage was 100–200 mV (the circles in Fig. 7), similar gap distances (1.3 ± 0.8 nm) were obtained from NCs having initial widths less than 6 nm. However, for higher fracture voltages (200–300 mV), gap distances ranged between 3 and 13 nm. Gaps with distances larger than 7 nm were produced from NCs having initial widths larger than 6 nm, except a gap of 7.3 nm that started from an initial width of 3.1 nm. This exceptional gap was produced from an NC that was longer than the others; the dissipation of the long thin region by EM led to formation of a wider gap, even though the initial width was smaller than 6 nm.

4. DISCUSSION

4.1. The Relationship Between Fracture Bias Voltage and Nanogap Distance

For the lowest bias voltage range (45–100 mV), the external shape of the NCs changed owing to EM, as observed by HRTEM. This shape change was represented by fluctuations in the conductance and the minimum cross-sectional area, as shown in Figure 2. Thus, the NCs did not break, even though EM occurred. This implies that thinning due to outflowing of atoms from the NC was recovered by inflowing atoms to the NC.

By applying higher bias voltages to the NCs (100–300 mV), nanogaps were produced. Thus, the amount of outflowing atoms from an NC was larger than that of the inflowing atoms to the NC, resulting in shrinkage of the NC followed by fracture. We can classify the relationship between the fracture bias voltage and the resulting nanogap distance according to two ranges of fracture bias voltages: 100–200 mV and 200–300 mV. For lower voltages (100–200 mV), the nanogap distances were similar.
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(1.3 ± 0.8 nm) regardless of the initial width of NCs up to 6 nm, as shown in Figures 6 and 7. The fluctuation in the minimum cross-sectional area during EM was 0.9 nm² at a fracture bias voltage of 100 mV. These values imply that shrinkage of the NC due to EM was localized in this narrow region. At higher fracture voltages (200–300 mV), the gap distances were distributed over a wider range (3–13 nm). The gap distances increased with increasing fracture voltage; however, the distances do not depend on the initial width of the NCs, as shown in Figure 7. The fluctuation in the minimum cross-sectional area during EM was approximately 9 nm² at a fracture bias voltage of 300 mV. The fluctuation frequency also increased, as described for Figure 4 (time c). Thus, both the speed and amount of EM in this voltage range became larger. Electron wind forces increase with bias voltage and cause acceleration of EM in this voltage range. At higher fracture voltages (200–300 mV), the shrinkage of the NC due to EM was localized in this narrow region. At higher fracture voltages (200–300 mV), the distances do not depend on the fracture bias voltage as they do in the range of lower fracture voltages. In contrast to EM, thermal atomic diffusion proceeds until cooling of the broken nanotips even after fracture. Thermal atomic diffusion increases with a rise in temperature. The temperature of NCs is determined by a balance between thermogenesis at NCs due to EM and thermal dissipation to electrodes beside the NCs. It is inferred that the expansion of nanogaps produced at 200–300 mV can be attributed to the temperature rise of the NCs.

4.2. The Nanogap Distance and Corresponding Molecules

Nanogaps have been used to sandwich single molecules, resulting in the formation of SMJs. We found that nanogaps with distances of 1.3 ± 0.8 nm and 3–13 nm can be produced over two different ranges of fracture voltage. The former nanogap distances correspond to such molecules as benzene, C₆H₆, and pentacene. The latter distances are comparable to such molecules as DNA, p-phenylene ethynylenes, and p-phenylene vinylene. Depending on molecular sizes, corresponding nanogaps can be produced using the EM method, and then SMJs can be assembled.

5. CONCLUSION

We used in situ HRTEM to investigate the formation of Ag nanogaps by EM. The critical voltage of EM in Ag NCs was approximately 45 mV. The relationship between fracture bias voltages and nanogap distances was classified into two voltage ranges: 100–200 mV and 200–300 mV. For the lower voltage range, nanogap distances of 1.3 ± 0.8 nm were obtained from NCs having widths smaller than 6 nm. For the higher voltage range, the nanogap distances ranged from 3 to 13 nm, regardless of NC width (2–9 nm). Thus, it was demonstrated that nanogap distances corresponding to molecular sizes can be controlled by selecting appropriate fracture bias voltages and NC widths.

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References and Notes


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