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Athermal Solid Phase Reaction in Pt/SiO_x Thin Films Induced by Electron Irradiation

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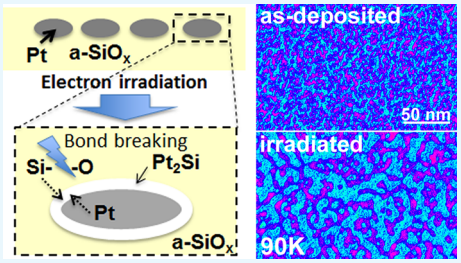
ABSTRACT: Microelectronics based on Si requires metal silicide contacts. The ability to form platinum silicide (Pt_2Si) by electronic excitation instead of thermal processes would benefit the field. We studied the effects of electron irradiation on Pt_2Si formation in composite films—composed of Pt and amorphous silicon oxides (a-SiO_x)—by transmission electron microscopy and electron diffraction. Pt_2Si formed in Pt/a-SiO_x bilayer and a-SiO_x/Pt/a-SiO_x sandwiched films by 75 keV electron irradiation, at 298 and 90 K. The reaction is attributable to dissociation of SiO_x triggered by electronic excitation. In a-SiO_x/Pt/a-SiO_x sandwiched films, reflections of pure Pt were not present after irradiation, i.e., Pt was completely consumed in the reaction to form Pt_2Si at 298 K. However, in Pt/a-SiO_x bilayer films, unreacted Pt remained under the same irradiation conditions. Thus, it can be said that the extent of the interfacial area is the predominant factor in Pt_2Si formation. The morphology of Pt islands extensively changed during Pt_2Si formation even at 90 K. Coalescence and growth of metallic particles (Pt and Pt−Si) are not due to thermal effects during electron irradiation but to athermal processes accompanied by silicide formation. To maintain the reaction interface between metallic particles and the dissociation product (i.e., Si atoms) by electronic excitation, a considerable concomitant morphology change occurs. Elemental analysis indicates that the decrease in Si concentration near Pt is faster than the decrease in O concentration, suggesting formation of a Si depletion zone in the amorphous silicon oxide matrix associated with formation of Pt_2Si.



INTRODUCTION

Metal silicides are indispensable contact materials in current Si-based microelectronics technology, and hence, much research focuses on their formation mechanism and phase stability.[1] Researchers commonly study transition metal silicides as thermoelectric devices as well.[2] A solid phase reaction of a metallic element with Si is the most popular manufacturing method for metal silicides. State variables (e.g., pressure, temperature, and activities of the components) determine the reaction equilibrium, and the Gibbs free energy change informs one as to whether or not a reaction is favorable. In general, Si is highly chemically active; some metallic elements (e.g., Ni, Pd, and Pt) that contact with pure Si form silicides at relatively low annealing temperatures.[3] All these phenomena correspond to a thermally activated atomic reaction.

However, atomic reaction induced by electronic excitation is another route to promote a solid phase reaction. However, there are few examples of such reactions in inorganic materials except the following two cases: (i) decomposition of GaSb nanoparticles by 25 keV electron irradiation[4] and (ii) Pt_2Si formation at a Pt/amorphous silicon oxide (a-SiO_x) interface by electron irradiation (25−200 keV)[5−7] or photoirradiation (140 eV).[6,8] These reactions proceed under irradiation conditions where knock-on atomic displacement is absent,[9] and hence, the origin of the atomic reaction is attributable to electronic excitation. Particularly in the latter case (Pt_2Si formation), a direct reaction between Pt and SiO_x by thermal annealing cannot occur, as experimentally confirmed.[5] The observed Pt_2Si formation is attributable to inner-shell electronic excitation.[6] Auger decay of a core hole in Si 2p electrons corresponds to decomposition of a-SiO_x, and hence, the dissociation product (i.e., Si atoms) may react with Pt. This reaction mechanism completely differs from that of the conventional, thermal interfacial reaction between Pt and pure Si.[10,11] The solid phase reaction by electronic excitation has potential applications to microfabrication because the metal silicide selectively forms only in the irradiated area. To understand the mechanism of Pt_2Si formation induced by electronic excitation, the role of the Pt/a-SiO_x interfacial area must be clarified.

We therefore studied the effects of electron irradiation on Pt_2Si formation in composite thin films composed of Pt and a-SiO_x using transmission electron microscopy (TEM) and

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electron diffraction. We emphasize the effects of the interface and reaction temperature on Pt_2Si formation. We also discuss a possible reaction mechanism on the basis of the results.

RESULTS AND DISCUSSION

Electron Irradiation at 298 K. Figure 1a and Figure 1b show the bright-field (BF) TEM image and the corresponding

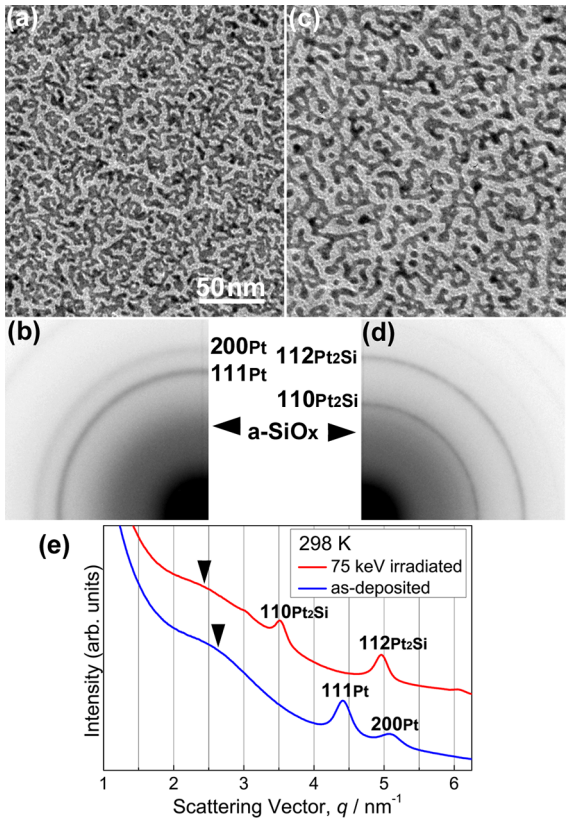

Figure 1. (a, b) BF−TEM images and SAED patterns, respectively, of an a-SiO_x/Pt/a-SiO_x composite film, as-deposited; (c, d) BF−TEM images and SAED patterns, respectively, of an a-SiO_x/Pt/a-SiO_x composite film, after 75 keV electron irradiation (carried out at 298 K for 3.6 ks); (e) intensity profiles of SAED patterns measured in the radial direction.

selected area electron diffraction (SAED) pattern, respectively, of an as-deposited a-SiO_x/Pt/a-SiO_x sandwiched film. Discontinuous island-like structures of Pt formed in the a-SiO_x matrix. The SAED pattern is composed of Debye−Scherrer rings of face-centered cubic Pt and a halo pattern of a-SiO_x. After 75 keV electron irradiation at 298 K for 3.6 ks, the morphology of the metallic particles (Pt or Pt−Si) considerably changed (Figure 1c). The electron dose rate was approximately 7.5×10^{22} electrons/m^2 s (hereafter, e/m^2 s). Particle coalescence and growth occurred during electron irradiation. The SAED pattern clearly shows a structural change after electron irradiation; α-Pt_2Si is formed (Figure 1d). Formation of α-Pt_2Si is consistent with the results of our prior study.[6] Silicide formation at the Pt/a-SiO_x interface does not occur thermally as mentioned in the Introduction (i.e., the Gibbs free energy change ΔG associated with the aforementioned silicide formation is positive, at least at temperatures between 298 and 873 K).[6] Instead, electronic excitation makes it possible to form Pt_2Si at the Pt/a-SiO_x interface.

Figure 1e shows intensity profiles measured in the radial direction of the SAED patterns of the specimens before and after electron irradiation (i.e., taken from Figure 1b and Figure 1d, respectively). We integrated the intensity in the circumferential direction. Formation of Pt_2Si after electron irradiation is clearly seen as reflections of Pt_2Si, and there are no reflections of Pt. Arrowheads indicate the peak position of the first halo ring of the a-SiO_x film. The peak shift toward lower spatial frequencies occurs after electron irradiation. This is consistent with the results of our previous study.[6] The peak shift is due to the change in the chemical composition of SiO_x (i.e., increase in the oxygen content) associated with Pt_2Si formation (Si depletion in SiO_x leads to an increase in the oxygen content).

Figure 2a compares the intensity profiles of the SAED patterns obtained for the Pt/a-SiO_x bilayer film and the a-

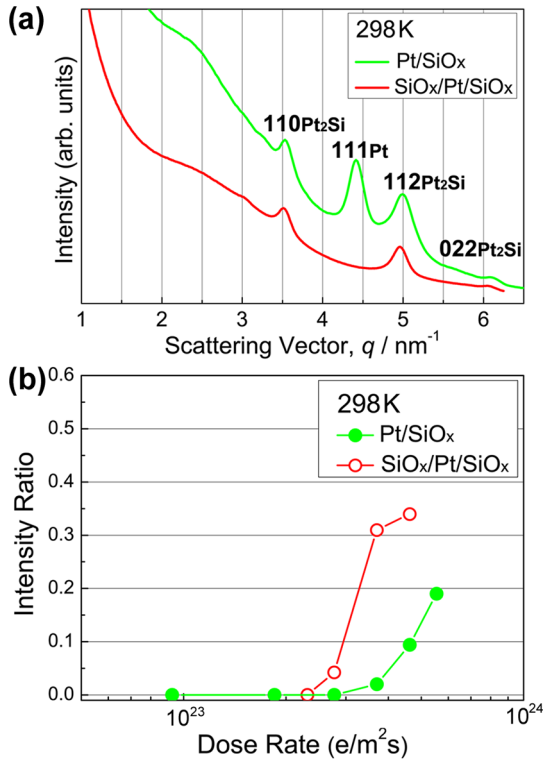

Figure 2. (a) Intensity profiles of the SAED patterns obtained for Pt/a-SiO_x and a-SiO_x/Pt/a-SiO_x composite thin films after 75 keV electron irradiation at 298 K for 3.6 ks. (b) Dose rate dependence of the integrated intensity ratios of 110_{Pt2Si} and 111_{Pt} reflections (I_{110}/I_{111}) at 298 K for 75 keV electrons.

SiO_x/Pt/a-SiO_x sandwiched film after 75 keV electron irradiation at 298 K for 3.6 ks. The electron dose rate was approximately 7.5×10^{22} e/m^2 s in both cases. A reflection of 111_{Pt} remains in the Pt/a-SiO_x bilayer film after electron irradiation, coexisting with newly formed reflections of Pt_2Si (green line). The presence of unreacted pure Pt indicates that the formation of Pt_2Si is still at an intermediate stage. However, Pt reflections were not present in the a-SiO_x/Pt/a-SiO_x sandwiched film (red line), namely, silicide formation has been completed in this specimen. We estimate the interfacial area between Pt and a-SiO_x in the a-SiO_x/Pt/a-SiO_x sandwiched film as roughly twice that of the Pt/a-SiO_x bilayer film; this interfacial area difference may have served as an essential factor in promoting the interfacial reaction. Assuming

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that the reaction rate is constant, the total quantity of reaction products proportionally depends on the interfacial area. All these considerations suggest that the extent of the interfacial area may correspond to the progress of Pt_2Si formation.

Figure 2b shows the dose rate dependence of the integrated intensity ratios of 110_{Pt2Si} and 111_{Pt} reflections (I_{110}/I_{111}) of the Pt/a-SiO_x bilayer film and of the a-SiO_x/Pt/a-SiO_x sandwiched film. We extracted the intensity ratios from the SAED patterns obtained using 75 keV electrons at 298 K. The irradiation time was 600 s for all the measurements. The dose rate of the order of 10^{23} e/m^2 s is 1 order higher than that used in Figure 1. The sandwiched film always shows a rapid increase compared with the Pt/SiO_x bilayer film within the dose rates used. This result also indicates that the quantity of reaction products depends on the extent of the interfacial area because the sandwiched film always shows a higher intensity ratio than the bilayer film regardless of the dose rate.

Electron Irradiation at 90 K. Figure 3a and Figure 3b show the BF−TEM image and the corresponding SAED pattern, respectively, of an as-deposited a-SiO_x/Pt/a-SiO_x sandwiched film observed at 90 K. The overall features of the microstructure are similar to those of the specimen shown in Figure 1a,b. An interesting microstructural feature observed here is that the morphology of the metallic particles also considerably changed at 90 K (Figure 3c). This result indicated that the coalescence and growth of metallic particles are not due to thermal effects during electron irradiation (beam heating) but to an electronic excitation effect, i.e., we ruled out a thermal process. There are conflicting reports regarding diffusing species during Pt_2Si formation at a Pt/pure Si interface. Pretorius[12] reported that Pt diffusion is dominant, whereas Poate and Tisone[13] reported that Si is the diffusing species. The dominant species are unknown in the case of Pt/a-SiO_x interfaces; however, to sustain the reaction, it is necessary to supply Si to the reaction front on the surface of the previously formed Pt−Si compound layer that exists between a metallic particle and an a-SiO_x matrix. In other words, it is conceivable that, to maintain the reaction front active at the interface between metallic particles (i.e., the Pt−Si alloy or compound particles) and a-SiO_x, the dissociation product (i.e., Si atom) from SiO_x should be steadily and constantly supplied to the front. One method of achieving such a supply is a drastic morphology change of the particles, which would facilitate a steady and constant supply of fresh surfaces of the Pt−Si metallic particles and consequently serve as a steady supply of new reaction sites where newly formed Si atoms may react with Pt atoms until the Pt atoms in the particles become saturated with respect to Si atoms. The considerable particle morphology change observed in Figures 1c and 3c may correspond to such a situation and may be attributable to the need to achieve a further free energy gain of the system. Such an appreciable morphology change is reminiscent of the extensive movement of metal particles during a catalytic reaction, e.g., *in situ* oxidation of graphene by Ag nanoparticles.[14]

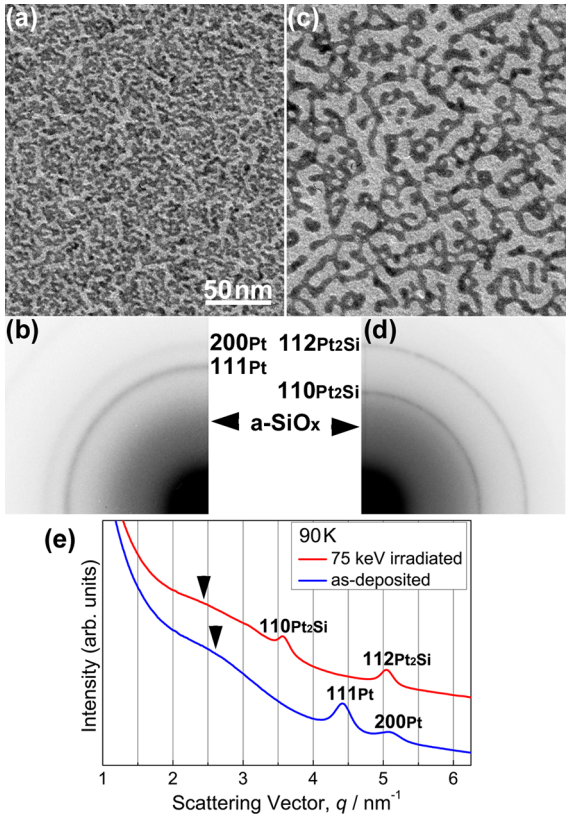

Figure 3. (a, b) BF−TEM images and SAED patterns, respectively, of an a-SiO_x/Pt/a-SiO_x composite film, as-deposited; (c, d) BF−TEM images and SAED patterns, respectively, of an a-SiO_x/Pt/a-SiO_x composite film, after 75 keV electron irradiation (carried out at 90 K for 3.6 ks); (e) intensity profiles of the SAED patterns measured in the radial direction.

Chemical Analysis by EDS Elemental Mapping. Figure 4a shows the STEM−EDS elemental map obtained for a cross-sectional specimen fabricated from an a-SiO_x/Pt/a-SiO_x sandwiched film grown on an Si(111) substrate. Si (red), SiO_x (purple), and Pt (green) layers are evident. We irradiated the specimen with 30 keV electrons for 10.8 ks (total dose: 1.7 × 10^{25} e/m^2) inside the dual-beam FIB prior to micro-sampling. A nanobeam electron diffraction pattern obtained from the α-Pt_2Si phase (Figure 4a, inset) shows that electron irradiation induced silicide formation. Pt-based metallic particles are dispersed, yet one cannot completely delineate the particles because of their overlap in the observation direction. A nanometer-scale rugged interface between Pt and SiO_x may favor appreciable atomic mixing during Pt_2Si formation. We infer that similar microstructures also formed in the specimens shown in Figures 1 and 3, because the sputtered Pt always forms islands on the a-SiO_x layer. Hence, it is presumed that the drastic change in the morphology of the metallic particles by electron irradiation, as observed in Figures 1c and 3c, takes place mainly in the lateral direction of the composite film, not in the film growth direction.

Figure 4b shows composition profiles extracted from the STEM−EDS map shown in Figure 4a. We quantified the concentration (in atomic percent) based on a thin film approximation[15] assuming the theoretical *k*-factor (standardless quantification), and hence, the derived concentrations are not quantitative.[16] We set the total Si, O, and Pt content to 100 at %. We assigned the origin of the distance to the Si/a-SiO_x interface, and the scale on the horizontal axis is the same in Figure 4a,b. The Si concentration started to decrease at approximately 32 nm (arrow 1), reached a minimum at 40 nm (center of the Pt location), and again increased and recovered at 50 nm (arrow 2). This change in the Si concentration profile may reflect the Pt_2Si formation at the rugged interface between Pt and SiO_x mentioned above. The oxygen content detected at

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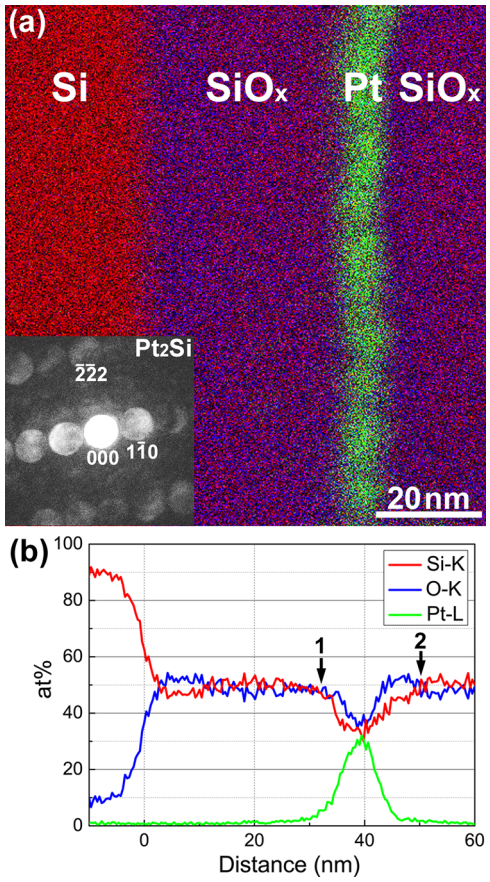

Figure 4. (a) STEM−EDS elemental map of the cross section of a-SiO_x/Pt/SiO_x/Si(111). We irradiated the sample with 30 keV electrons at room temperature for 10.8 ks. The inset shows a nanobeam electron diffraction pattern obtained from the α-Pt_2Si phase. (b) Composition profiles extracted from the STEM−EDS map. Arrows 1 and 2 indicate the positions where the Si concentration decreases and subsequently increases, respectively. The Si on the surface of the cross-sectional specimen may be covered with a native oxide.

the Pt layer is due to the overlap of Pt (or Pt−Si) and SiO_x in the projection direction in the cross-sectional TEM observation.

Figure 5 shows the schematic of Pt_2Si formation at the Pt/a-SiO_x interface by electron irradiation. Electronic excitation first breaks a Si−O bond, which is immediately followed by Pt−Si bond formation at the Pt/a-SiO_x interfaces,[6] and eventually, Pt_2Si formation leads to Si depletion in the SiO_x matrix. This Si depletion was also detected in an electron diffraction study.[6] Regarding the atomic concentration imbalance in electron-irradiated amorphous silicon oxide, Chen et al. reported that a 100 keV electron irradiation of amorphous SiO_2 results in oxygen deficiency due to a combination of sputtering, surface desorption, and a volume-dissociated mechanism.[17] This does not agree with our results. The difference may be attributable to the presence (the present work) or absence (Chen et al.[17]) of embedded Pt particles. Researchers have reported atomic-scale disproportionation in a-SiO; in this case, a-Si-like and a-SiO_2-like clusters are present in a-SiO.[18] Although our results are based on electron microscopy experiments, the effect of electronic excitation on dissociation of the Si−O bond, which we verified here and in recent studies,[6,8] is not explicitly incorporated in the above-mentioned paper.[18]

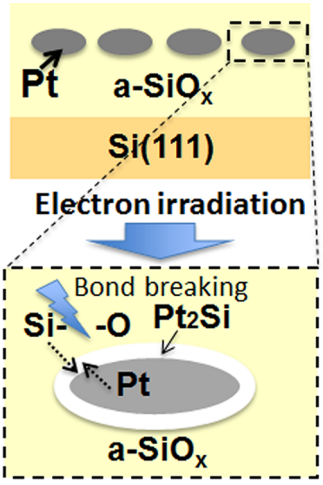

Figure 5. Schematic of Pt_2Si formation at the Pt/a-SiO_x interface by electron irradiation.

CONCLUSIONS

We studied the effects of electron irradiation on Pt_2Si formation in composite thin films composed of Pt and a-SiO_x using TEM and electron diffraction. Pt_2Si formed in both Pt/a-SiO_x bilayer and a-SiO_x/Pt/a-SiO_x sandwiched films by 75 keV electron irradiation, at 298 and 90 K. It becomes clear that the extent of the interfacial area between Pt and a-SiO_x is the predominant factor in the progress of Pt_2Si formation. Pt_2Si formation induced by electronic excitation occurs even at 90 K, suggesting that an athermal atomic process is involved in Pt_2Si formation and growth. We infer that, to maintain the reaction interface between the metallic particles (Pt or Pt−Si) and the dissociation product (i.e., Si atoms) of SiO_x by electronic excitation, a considerable concomitant particle morphology change occurs. The remaining question seems how the Si depletion zone forms in a-SiO_x, and how it is related to silicide formation. Hence, further study is necessary on the atomic mechanism of the solid-phase reaction under electronic excitation.

MATERIALS AND METHODS

Specimen Preparation. Composite films of Pt and a-SiO_x (hereafter, Pt/a-SiO_x) were prepared by dc magnetron sputtering of Pt onto an a-SiO_x film kept at room temperature, which was formed by vapor deposition of silicon monoxide SiO on cleaved NaCl(001) substrates or on Si(111) wafers prior to the sputtering of Pt. The oxygen content, x, in the a-SiO_x film was approximately 1.5 ($SiO_{1.5}$), as determined in a prior study.[5] Some of the specimens were further coated by a-SiO_x to prepare Pt islands embedded between a-SiO_x films (i.e., sandwich-type a-SiO_x/Pt/a-SiO_x). Both types of composite films prepared on NaCl substrates were then floated on distilled water and mounted onto copper grids for TEM experiments. One can find details of the specimen preparation procedures elsewhere.[5−7] Cross-sectional TEM specimens of the a-SiO_x/Pt/a-SiO_x sandwiched film were prepared from the composite films on Si(111) wafers using a focused ion beam (FIB) instrument (Thermo Fisher Scientific Scios2 Dual Beam).

Electron Irradiation and TEM Observations. The composite films on copper grids were irradiated with 75 keV electrons using a transmission electron microscope (TEM)

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(Hitachi H-7000). The electron dose rate was estimated using a Faraday cage attached to the TEM. Irradiation was carried out at 298 and 90 K for 3.6 ks. Some of the specimens, such as cross sections of a-SiO_x/Pt/a-SiO_x/Si(111), were characterized using a 200 kV TEM (JEOL JEM-ARM200F). All the TEM images and SAED patterns were recorded using 2 k × 2 k charge-coupled device cameras (Gatan Orius and Ultra-Scan1000). Compositional analysis was performed in scanning transmission electron microscopy (STEM) mode using energy-dispersive X-ray spectrometry (EDS; JEOL JED-2300) attached to the 200 kV TEM. For STEM−EDS analysis of the cross-sectional specimens, the Pt layer was placed orthogonal to the tilt axis of the specimen holder and tilted 10° toward the EDS detector.

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Author Contributions

All authors contributed to the discussion and writing of the manuscript. The final version of the manuscript was approved by all authors.

Notes

The authors declare no competing financial interest.

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