In situ observation of the irradiation induced structural change at palladium/silicon oxide (Pd/SiO$_x$) interfaces under electron irradiation focusing on the temperature dependence

T. Nagase$^{1,2}$, R. Yamashita$^2$, J.-G. Lee$^3$

$^1$Research Center for Ultra-High Voltage Electron Microscopy, Osaka University, 7-1, Mihogaoka, Ibaraki, Osaka 567-0047, Japan
$^2$Division of Materials and Manufacturing Science, Graduate School of Engineering, Osaka University, 2-1, Yamada-Oka, Suita, Osaka 565-0871, Japan
$^3$Powder & Ceramics Division, Korea Institute of Materials Science, 66 Sangnam-dong, Changwon, Kyungsangnam-Do 641-101, Korea

Electronic excitation by electron beams can modify the structure and properties of materials. It has become clear that excitation can provide novel types of modifications with better-controlled changes. In situ TEM observation of the electron irradiation-induced structural change is the most useful technique for elucidating the structural changes induced by electron-beam irradiation and consequent electronic excitation in materials. For materials modification through electronic excitation at metal/amorphous-silicon oxide (SiO$_x$) interfaces by electron-beam irradiation, epitaxial growth of Pt$_2$Si on Pt in Pt/SiO$_x$ [1, 2], amorphous phase formation [3,4], and Pd$_2$Si formation after the amorphous phase formation [5] in Pd/SiO$_x$ has been reported. To clarify the irradiation-induced structural change in metal/SiO$_x$ in detail, the temperature dependence of the irradiation-induced structural change in Pd/SiO$_x$ was investigated.

The preparation of Pd/SiO$_x$ specimens has been described in detail in literature [3,4]. Electron irradiation was performed using Hitachi H-800 at an acceleration voltage of 200 keV and a dose rate of $4.4 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$ between 298 K and 873 K. Electron irradiation above 298 K was performed using a single-tilt-type heating holder, Hitachi H-500H.

Figure 1 shows the change in bright-field (BF) images and the corresponding selected area diffraction (SAD) patterns of Pd/SiO$_x$ interfaces at 298 K (Fig. 1a–1c) and at 873 K (Fig. 1d–1f). At 298 K, before irradiation, the BF image and SAD pattern show that the Pd nanoparticles were oriented towards [001] on SiO$_x$ (Fig. 1a). After irradiation for $2.4 \times 10^3$ s, a change in the shape of the nanoparticles, disappearance of crystalline contrast in the BF image, and the appearance of a halo ring indicated by index A in the SAD pattern were observed (Fig. 1b). On further irradiation, the shape of the nanoparticles change to the faceted shape shown in the BF image and discontinuous Debye rings appear with the disappearance of halo ring A in the SAD pattern, as shown in Fig. 1c. This was explained by amorphous Pd-Si formation [3,4] and subsequent Pd$_2$Si silicide formation [5]. The irradiation-induced structural change was also observed at 873 K. Before irradiation, Pd nanoparticles oriented towards [001] on SiO$_x$ were observed (Fig. 1d), indicating that annealing-induced structural change did not occur in Pd/SiO$_x$. After 300 s of irradiation, grain coarsening of Pd nanoparticles and the disappearance of crystalline contrast were observed in the BF image (Fig. 1e). A broad halo ring indicated by the index B appeared simultaneously with the disappearance of the diffraction spot corresponding to Pd in the SAD pattern, indicating amorphization. Additional change in the BF image and the SAD pattern was observed...
with the increase in the irradiation time after amorphization. For the specimen irradiated for \(1.2 \times 10^3\) s, a change in the shape of particles and the appearance of crystalline contrast were seen in the BF image (Fig. 1f). In the SAD pattern, the halo ring B vanished completely and a new discontinuous Debye ring appeared. The two-step structural change behavior in Pd/SiO\(_x\) under irradiation at 873 K can be explained by the formation of an amorphous phase and the subsequent crystallization leading to the formation of Pd\(_2\)Si. The crystallization temperature \(T_x\) of the Pd\(_{80}\)Si\(_{20}\) melt-spun amorphous specimen evaluated at a heating rate of 0.67 K·s\(^{-1}\) was 679 K [5].

Amorphous phase formation at a temperature above \(T_x\), and the difference in the crystallization behavior between thermal crystallization [5] and electron irradiation-induced crystallization of a Pd-Si amorphous phase on SiO\(_x\) indicates that the irradiation-induced amorphous phase formation and crystallization of an amorphous phase does not occur by the thermally activated metallurgical reaction but by an electron stimulated mechanism under irradiation.

References

\[
\begin{align*}
T = 298 K & \quad T = 873 K \\
(a) & \quad 0 \text{ s} & \quad (d) & \quad 0 \text{ s} \\
(b) & \quad 9.4 \times 10^3 \text{ s} & \quad (e) & \quad 300 \text{ s} \\
(c) & \quad 5.4 \times 10^3 \text{ s} & \quad (f) & \quad 1.2 \times 10^3 \text{ s} \\
\end{align*}
\]

FIG. 1. Change in BF images and corresponding SAD patterns of Pd/SiO\(_x\) interfaces at 298 K ((a), (b), and (c)) and at 873 K ((d), (e), and (f)). Electron irradiation was performed at an acceleration voltage of 200 keV and a dose rate of \(4.4 \times 10^{23} \text{ m}^{-2} \cdot \text{s}^{-1}\). Debye rings in Figs. 1c and 1e can be identified as Pd\(_2\)Si with a hexagonal structure belonging to the space-group \(hP9\).