The Effect of Annealing Temperature on The Formation of Silicides Phase of Nanoindented Ag/Si Thin-Film

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Abstract - The effect of annealing temperature on the formation of silicides phase of nanoindented Ag/Si thin-film is investigated. Ag films with a thickness of 500 nm are deposited on (100) silicon substrates. Nanoindentation is performed to a maximum depth of 800 nm, and the indented specimens are then annealed at temperatures of 600℃, 700℃ and 800℃, respectively. In the as-deposited specimen, the indentation process results in a phase transformation from a diamond cubic structure to amorphous phase within the indented zone. Following annealing at 600℃, the microstructure of the indented zone changes from a fully-amorphous state to a mixed amorphous / nanocrystalline state. Consequently, the microstructures of the indentation zones in the specimens annealed at 700℃ and 800℃, respectively, contain a mixture of amorphous phase, nanocrystalline structures and Ag_2Si silicide phase.

Keywords - Nanoindentation, Ag/Si thin film, Annealing, Ag2Si silicide phase.

I. INTRODUCTION

Silicon is one of the most commonly used substrate materials in the microelectronics and optoelectronics industry due to its excellent semiconducting properties. Face-centered cubic (fcc) films deposited on silicon substrates are widely used as metallic contacts at the micro- and macro-scales [1]. Previous studies have examined the microstructural transformation within the nanoindentation zone of thin-film systems by means of Raman spectroscopy, scanning/atomic force microscopy, and transmission electron microscopy (TEM) using either plane-view or cross-sectional specimens. In general, the results have shown that the plastic deformation and phase transformation induced during the nanoindentation of thin films are temperature dependent. Furthermore, it has been shown that the indented microstructure of an as-deposited specimen can be modified via annealing at a suitable temperature [2, 3]. Furthermore, for thin films deposited on a silicon substrate, various types of silicide are commonly formed at the film / substrate interface during subsequent annealing [4]. Therefore, in developing thin film systems for device applications, a thorough understanding of the nanoindentation behavior and microstructural evolution of thin film structures during nanoindentation and annealing is required.

Although the nano-indentation properties of Ag/Si thin films and the characteristics of Ag/Si silicides compound have been studied [4, 5], the combined effects of nanoindentation deformation and annealing on the microstructural evolution and the formation of silicides phase of Ag/Si thin films are not yet fully understood. Accordingly, this study uses a nanoindentation technique to examine the nano-mechanical properties of as-deposited Ag/Si thin films indented to a depth of 800 nm. The effects of the annealing temperature on the microstructural evolution and formation of Ag_2Si silicide phase within the nanoindented specimens are then examined using transmission electron microscopy (TEM) and X-ray Diffractometer (XRD).

II. EXPERIMENTAL PROCEDURE

Polycrystalline Ag films with a thickness of 500 nm were deposited on Si (100) wafers. The Ag films were deposited using a thermal evaporation technique under high vacuum conditions (10^{-6} torr). The nanoindentation tests were performed at room temperature using an MTS Nano Indenter-XP system with a Berkovich diamond pyramid tip. In order to realize the interaction between the Ag atoms and the silicon substrate and the formation of silicides phase within the indentation affected zone, the specimens were indented to a maximum depth of 800 nm using the indenter system set in a depth-control mode. The hardness and Young's modulus of the as-deposited Ag/Si thin film were then calculated from the loading-unloading curve using the Oliver and Pharr method [6]. Following the nanoindentation tests, selected specimens were annealed at temperatures of 600℃, 700℃ or 800℃ for 2 min in a rapid thermal annealing (RTA) furnace. Thin foil specimens for TEM observations were prepared from the as-deposited and annealed samples using an FEI Nova 200 focused ion beam (FIB) system with an operating voltage of 30 keV. The TEM foils were milled from the thin-film specimens using a Ga^+ ion beam and were extracted in such a way that they contained the centre of the indentation zone. The TEM specimens were placed on a copper net using a vitreous needle and were held in place via van der waals forces. The copper net was placed in the TEM chamber and the microstructure of the indentation region was observed using a Philips Tecnai F30 electron microscope. The chemical compounds observed at various positions of the as-deposited and annealed samples were identified using an EDAX energy dispersive X-ray spectrometer. Finally, the nature of the Ag silicide phase formed within the indented zone under each annealing temperature is identified using a computer-controlled X-ray Diffraction system (PW 3040/60).

III. RESULTS AND DISCUSSION

A. Loading-Unloading Curve

Figure 1 shows the loading-unloading curve of the as-deposited Ag/Si thin film. It can be seen that the loading part of the curve is continuous and smooth without any pop-in event. For indentation depths of less than 50 nm, the indenter tip is fully enclosed within the Ag film. The film has a low hardness and is easily deformed, and thus the load is very small and remains virtually constant. However as the indentation depth is increased, the indenter penetrates through the Ag layer and enters the underlying, harder Si substrate. As a result, the load increases rapidly toward a maximum value of 28.5 mN at the maximum indentation depth of 800 nm. This value is less than the critical load of 30 mN associated with the pop-out event for hard Si substrates [7]. As a result, the unloading portion of the curve in Fig 1 has a smooth gradient. Moreover, the presence of a slight elbow feature in the final portion of the unloading curve suggests that the silicon substrate transforms from a diamond cubic like structure to an amorphous structure in the indentation affected zone. It is noted that as the indentation depth is less than 800 nm, amorphous nature still remains within the indentation affected zone due to the absence of pop-out event. According to the load-displacement data shown in Fig. 1, the hardness and Young's modulus of the Ag/Si thin film are calculated as 2.1 GPa and 158 GPa, respectively, at the maximum depth of 800 nm. For the Zr-Cu-Ti thin film [2], after annealing at 473K and 563K for 1h, the film still remains amorphous. In addition, the Young's modulus of Au and Pt/Cu film is measured as 88.6 GPa and 123.4 GPa, respectively[3]. Note that an increase of Ag film thickness leads to a decrease of hardness and Young's modulus of the Ag/Si thin film. Furthermore, under a constant indentation depth and annealing temperature, the diffusion activity of the Ag atoms into Si substrate decreases with increasing Ag film thickness.

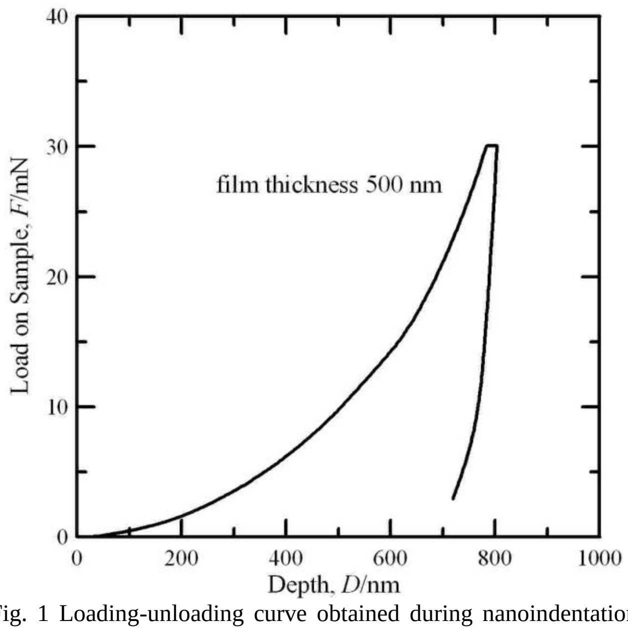


Fig. 1 Loading-unloading curve obtained during nanoindentation of as-deposited Ag/Si thin film.

B. Initial and Indented Microstructures of As–Deposited Ag/Si Thin Films

Figure 2 presents a TEM micrograph of the as-deposited Ag/Si thin film prior to indentation. A well-defined boundary is observed between the Ag film and the Si substrate. As shown in the selected area diffraction (SAD) patterns in the upper-right and lower-right corners of Fig. 2, the Ag thin film (B) has a polycrystalline structure while the silicon substrate (A) has a single crystal structure.

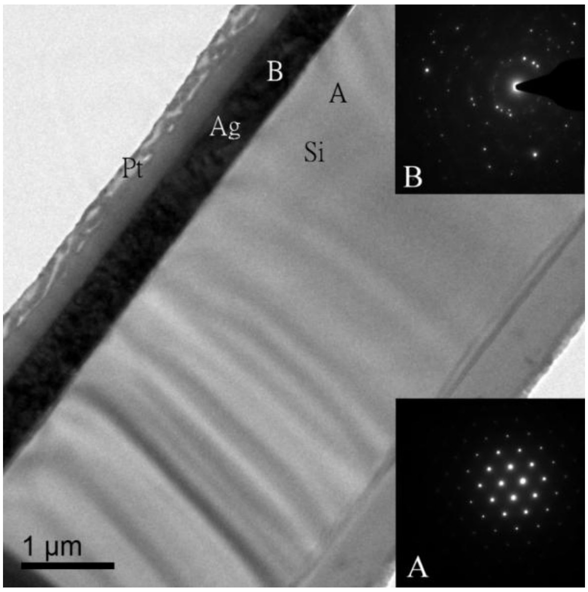
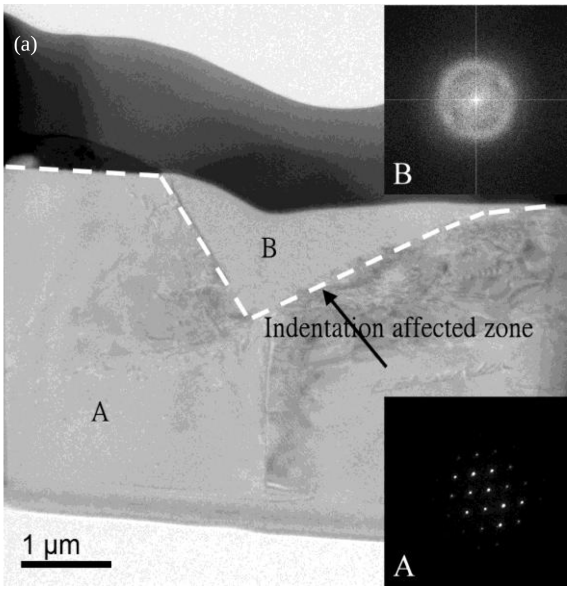


Fig. 2 Bright field TEM micrograph of as-deposited Ag/Si thin-film.

Figure 3(a) presents a cross-sectional TEM micrograph of the as-deposited Ag/Si specimen indented to 800 nm. The insets in the lower-right and upper-right corners of the figure show the TEM diffraction patterns of regions A and B, respectively. The results show that the silicon substrate has a diamond cubic structure while the indentation affected zone comprises amorphous phase. Fig. 3(b) presents a high-resolution TEM micrograph of the indentation affected zone. As discussed in Section A, the change from a diamond cubic structure to fully-amorphous phase in the indentation affected zone is thought to account for the elbow feature observed in the final portion of the unloading curve obtained in the nanoindentation test.



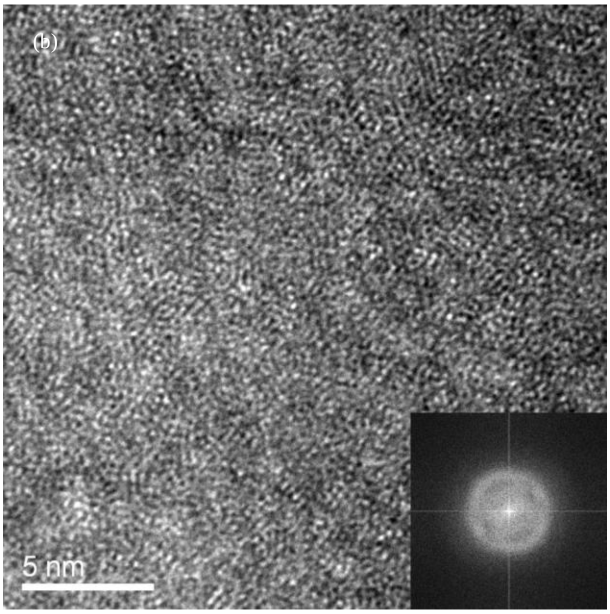
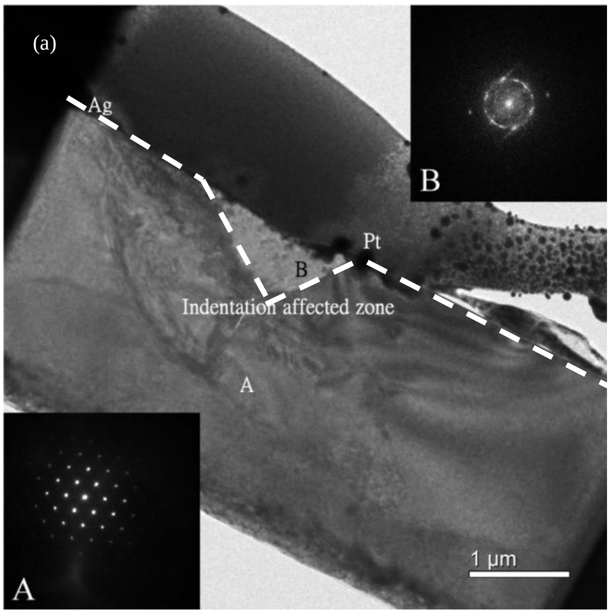


Fig. 3 (a) Bright field TEM micrograph of as-deposited indented specimen; (b) high-magnification micrograph of Si substrate; (b) high-magnification micrograph of indentation affected zone.

C. Indented Microstructure Following Annealing at Different Temperatures

Figure 4(a) presents a cross-sectional TEM micrograph of the indented Ag/Si specimen annealed at a temperature of 600℃. The insets in the lower-left and upper-right corners of the figure show the TEM diffraction patterns of the silicon substrate (A) and indentation affected zone (B), respectively. Figure 4(b) shows that the annealing temperature causes the microstructure in the indentation affected zone to change from a fully-amorphous state to a mixed amorphous / nanocrystalline state. The silicide phase does not form at lower annealing temperature of 600℃, implying that the diffusion activity between Ag atoms and silicon substrate is in sufficient.



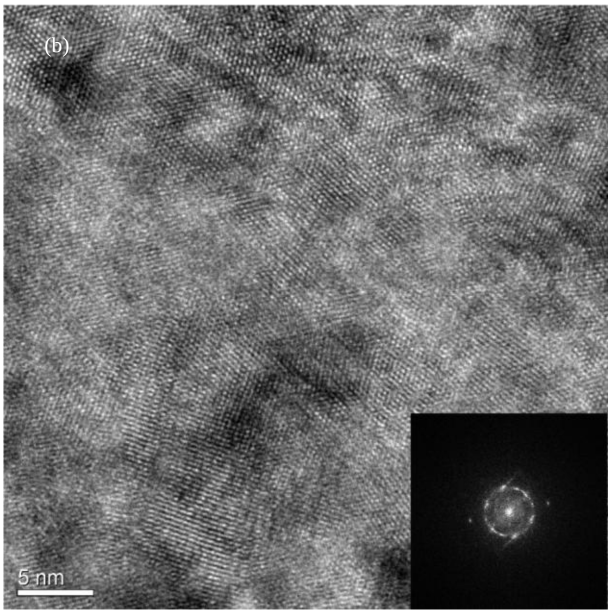
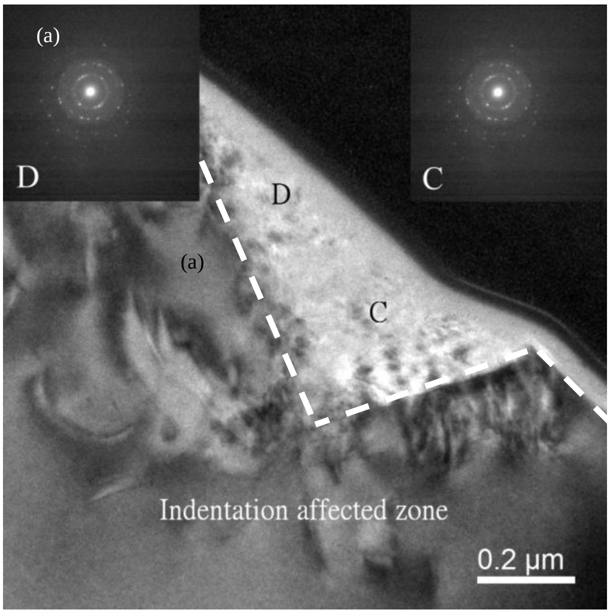
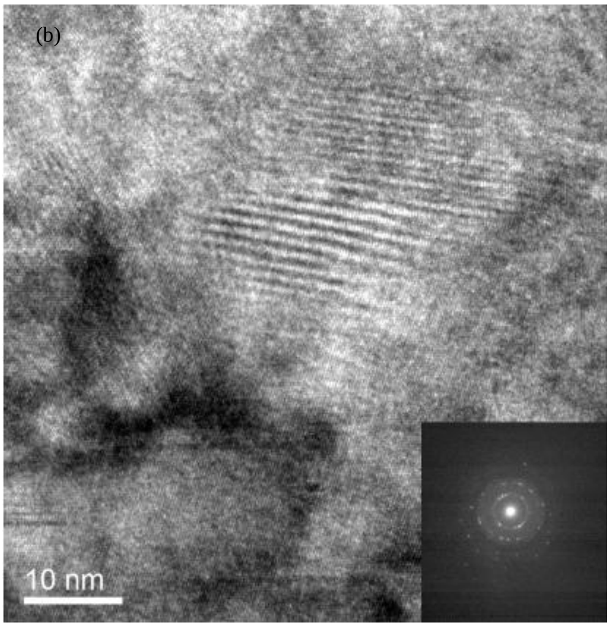


Fig. 4 (a) Bright field TEM micrograph of indented specimen annealed at 600℃ for 2 min; (b) high-magnification micrograph of indentation affected zone.

Figure 5(a) presents a TEM micrograph of the indented Ag/Si specimen annealed at 700°C. In contrast to the as-deposited indented specimens and the specimens annealed at temperature of 600℃, the current specimen contains Ag2Si silicide phase in the indentation affected zone. The elevated annealing temperature causes the reconstruction of Si either the Si atom diffuse into the Ag layer or diffusion of Ag into the Si layer to form silver silicide compounds. Thus, as shown in Fig. 5(b), corresponding to region C in Fig. 5(a), the indentation affected zone contains Ag_2Si silicide phase with a crystalline structure. Note that Ag_2Si silicide phase has an orthorhombic structure, with lattice parameters a=0.566 nm, b=0.916 nm, c=0.849 nm [8]. In addition, it can be seen that the matrix microstructure around the Ag2Si silicide phase contains a mixture of amorphous phase and nanocrystalline phase. The XRD measurement within the indentation affected zone confirms the presence of silicide compound and their crystallinity. The XRD spectra of the as-deposited indented specimen and the indented specimens annealed at temperatures of 600℃, 700℃, and 800℃ are shown in Fig. 5(c). As observed, Ag_2Si, Ag and Si peaks are formed at 32.31^o, 38^o and 70^o, respectively. It is noted that grazing incidence X-ray diffraction (GIXRD) measurments show the formation of Ag_2Si for irradiation at 400℃[4].

Figure 6(a) presents a TEM micrograph of the indented Ag/Si specimen annealed at a temperature of 800℃. Fig. 6(b) corresponding to region B in Fig. 6(a) shows that the indentation affected zone contains a mixture of amorphous phase, nanocrystalline phase and Ag_2Si silicide phase. The peak of silver silicide becomes significantly stronger and sharper with increasing of annealing temperature as shown in Fig. 5(c). The intensity of the Ag_2Si silicide phase increases with increasing the annealing temperature due to the greater diffusion ability of the Ag atoms. As a result, the indentation affected zone contains a greater amount of Ag_2Si silicide phase than that in the specimen annealed at a lower temperature of 700℃. The increased presence of Ag_2Si silicide phase within the indentation affected zone can be attributed to the stronger diffusion effect induced by the higher temperature. The annealing processes and diffusion activity can be explained by the classical Arrhenius equation. The diffusion activity and diffusion reaction rate of the Ag atoms into the Si substrate both increase with increasing annealing temperature. The present study has shown that the formation of Ag_2Si silicide phase can also be induced by nanoindenting the Ag-Si system and then annealing the indented microstructure at a temperature of 700℃ (or above). This phenomenon can be explained by the fact that nanoindentation causes a significant distortion of the lattice structure within the indented zone. During annealing, the distorted crystalline structure results in an increased number of diffusion paths between the Ag layer and the Si substrate. Consequently, the diffusivity of the Ag atoms is enhanced, and crystallisation of Ag_2Si silicide phase occurs.





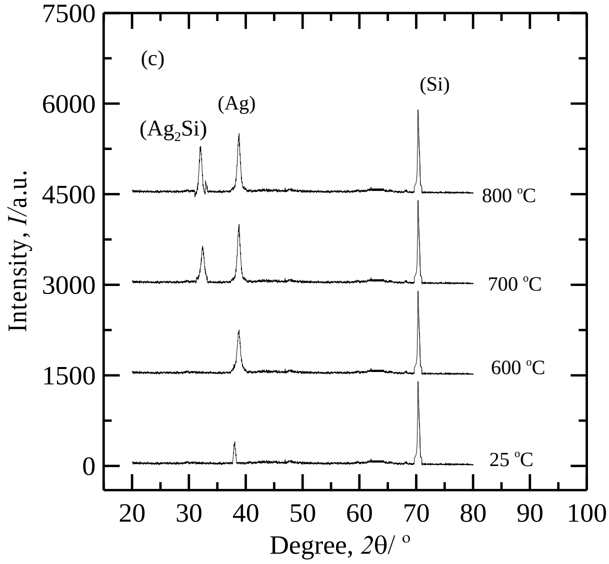
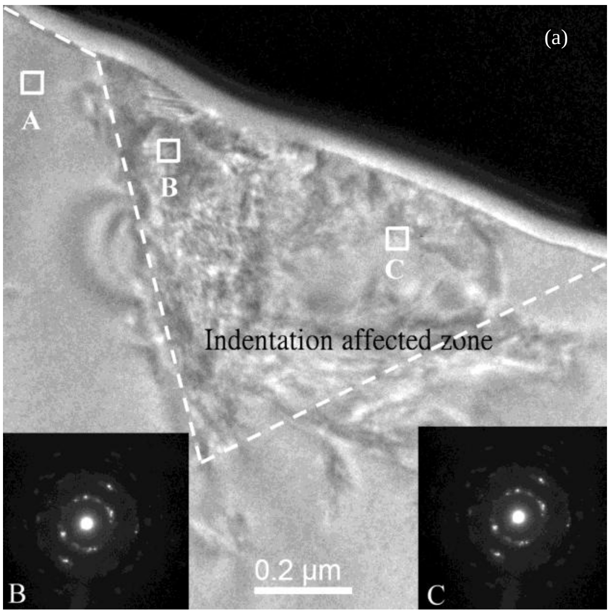


Fig. 5 (a) Bright field TEM micrograph of indented specimen annealed at 700℃ for 2 min; (b) high-magnification micrograph of indentation affected zone; (c) X-ray diffraction spectra of Ag/Si thin film at 25℃ and various annealing temperatures ranging from 600℃~800℃.

IV. CONCLUSION

The effect of the annealing temperature (600℃~800℃) on the formation of Ag-Si eutectic phase in the indentation affected zone of Ag/Si thin-film systems has been examined. The hardness and Young' s modulus of the as-deposited Ag/Si system are equal to 2.1 GPa and 158 GPa, respectively, at the maximum indentation depth of 800 nm. For all three annealing temperatures, i.e., 600℃, 700℃ and 800℃, the microstructure within the indentation zone is characterised by a mixed amorphous phase / nanocrystalline structure. In addition, for the specimens annealed at a temperature of 700℃ or more, the indentation zone also contains Ag_2Si silicide phase. The intensity of the Ag_2Si silicide phase increases with an increasing annealing temperature due to the greater diffusivity of the Ag atoms into the silicon substrate.



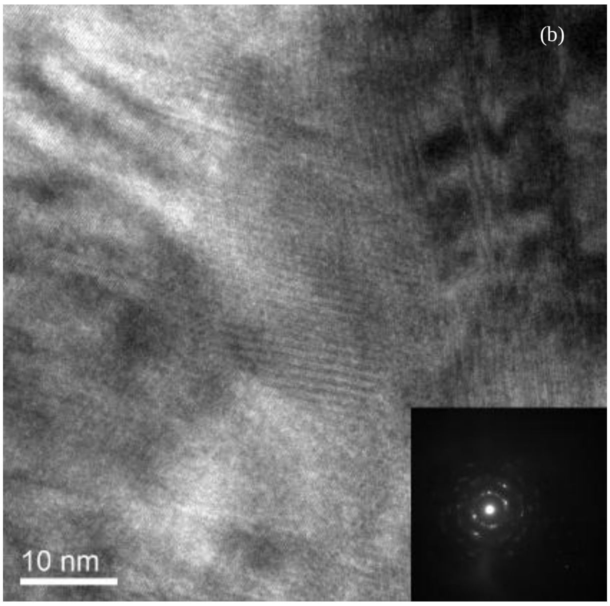


Fig. 6 (a) Bright field TEM micrograph of indented specimen annealed at 800℃ for 2 min; (b) high-magnification micrograph of region B in Fig. 6(a).

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