Direct observation of the formation of alumina phase by metallic Al solid-SiO_2 solid reaction

S. Sasaki, H. Suzuki, Y. Kimura, T. Sato, T. Tanigaki, O. Kido, K. Kamitsuji, M. Kurumada, and C. Kaito

Department of Nanophysics in Frontier Projects, Ritsumeikan University, Kusatsu-shi, Shiga 525-8577, Japan

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The formation of Al_2O_3 phases by the solid-solid reaction of a metallic Al layer evaporated on a SiO_2 amorphous grain has been induced by heating above 600°C in vacuum (1×10^{-6} Pa). The distortion process of the amorphous SiO_2 grains by the formation of Al_2O_3 have been directly imaged by in-situ TEM observation. A partly deposited Al layer covered the SiO_2 grains after heating at 750°C, and γ-Al_2O_3 grains of about 25 nm diameters were formed on the SiO_2 surface. Upon the growth of Al_2O_3, the SiO_2 grain decomposed into a mixture of metallic Si and SiO_2 and disappeared as a result of sublimation due to the formation of SiO_x at high temperatures. The present result on dust surface dynamics will become an important field with respect to the metamorphism of grains from the astromineralogical viewpoint.

Key words: Silicon oxide, alumina, solid-solid interaction, electron microscopy, diffusion, metamorphism.

1. Introduction

Both equilibrium condensation calculation (Grossman, 1972; Kornacki and Fegley, 1984) and nonequilibrium nucleation accompanying grain growth (Yamamoto and Hasegawa, 1977; Kozasa *et al*., 1989) indicate that corundum (Al_2O_3) grains are the first material to condense in the expanding and cooling gas of solar composition in an oxygen-rich atmosphere. The first-formed corundum is subsequently transformed, by reactions with gaseous Ca and Mg compounds, into spinel ($MgAl_2O_4$), hibonite ($CaAl_{12}O_{19}$) and other compounds at lower temperatures (Yamamoto and Hasegawa, 1977). However, numerous corundum grains were found in the Murchison CM2 chondrite (Anders *et al*., 1991; Virag *et al*., 1991) and identified as presolar material. Recent result of nano-secondary ion mass spectrometry also suggested in silicate presolar materials (Messenger *et al*., 2003; Nguyen and Zinner, 2004; Nagashima *et al*., 2004). Silicate grains in space have recently attracted the interest of many astrophysists due to the increasing amount and quality of observational data. In oxygen-rich envelopes, the most abundant elements available for grain formation are O, Fe, Si, Mg, Al and Ca. Without considering the kinetics of grain formation, we expect the presence of silicates, silica, corundum, spinel, iron and silicon grains. All of the refractory elements present in stellar outflow from evolved star will eventually condense as grains. The growth of silicate dust particles will probably be a trigger for the condensation of other supersaturated elements such as Mg, Fe and Al on the newly formed silicate surface, as suggested by the grain formation and metamorphism observed in experiments using SiO_x, FeO_x and AlO_x smoke (Nuth, 1996). IR spectra of these smoke materials after heat treatment suggested the growth of a corundum phase. The interdiffusion of Al and Si in solid state is the key on the metamorphism. But the fundamental phenomenon is hardly known. In the present study, the alteration process of amorphous SiO_2 dust to Al_2O_3 via the Al solid-SiO_2 solid reaction is directly observed using a transmission electron microscope (TEM).

2. Experimental Method

The starting material of silicon oxide (SiO_2) grains, which were spherical and amorphous, was produced from silicon powder using thermal plasma at a high pressure of 1.33 kPa in a gas mixture of O_2 (665 Pa) and Ar (665 Pa) (Sato *et al*., 2003). An aluminum layer with a mean thickness of 20 nm was evaporated onto some of the spherical SiO_2 grains which were then put on a glass slide. Since the SiO_2 grains were spherical, the Al grains were produced on one side of the SiO_2 grains, as shown in the schematic image in Fig. 1. The transmission IR spectra of the starting material, embedded in KBr pellets, were measured with a Fourier-transform infrared spectrometer (FTIR, Horiba FT210) over the wavelength region from 2.5 to 25 μm. These grains were heated in vacuum and examined using TEM, Hitachi H-7100R operated at 100 kv and H-9000NAR operated at 300 kv. These samples were observed in situ using a special heating holder attached to H-9000NAR, which can heat the grains to 1500°C in vacuum (10^{-6} Pa) (Kimura *et al*., 2000). The specimen was directly mounted on the conical tungsten heater. The dynamics of the specimen was recorded on videotapes.

3. Results and Discussion

The present SiO_2 grains were amorphous and had the diameter of 50–300 nm. Since the infrared spectrum exhibited absorption peaks at 8.9, 12.3 and 21 μm, the SiO_2

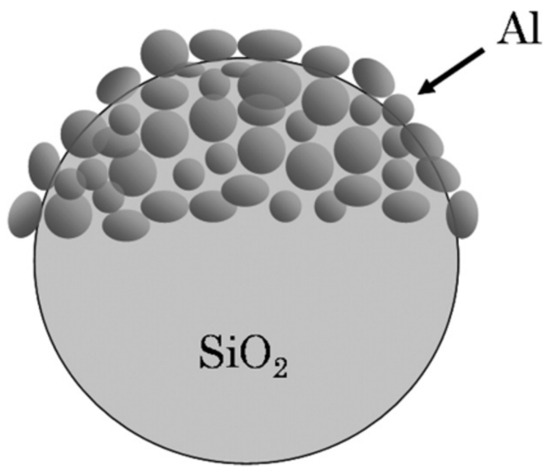

Fig. 1. Schematic of the initial Al film deposited on part of amorphous SiO_2 grain.

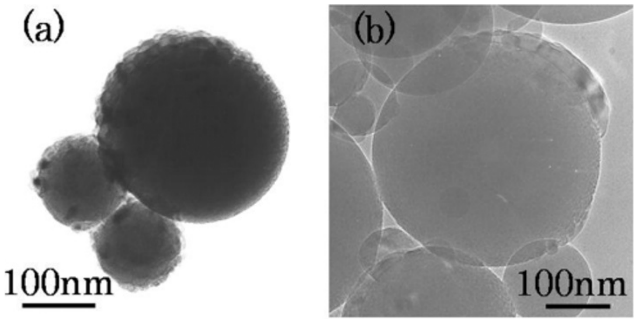

Fig. 2. (a) TEM image of the as-prepared specimen. (b) TEM image of the specimen after heating for 20 min at 600°C.

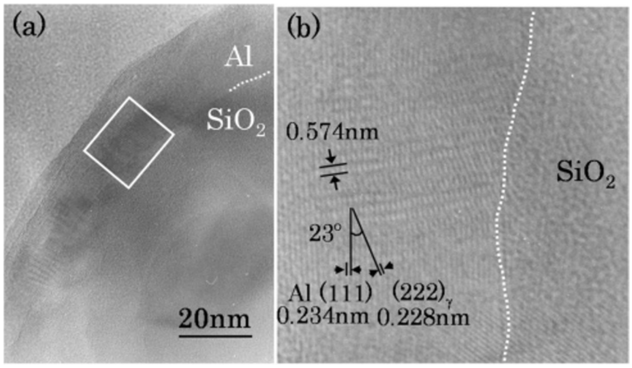

Fig. 3. HRTEM images of Al-deposited SiO_2 grain after heating for 20 min at 600°C. (b) Enlarged image of part of the interface in (a). The lattice images of Al and γ-Al_2O_3 can be seen. 0.574 nm fringes are Moiré by the double refractions between $(111)_{Al}$ and $(222)_{\gamma\text{-}Al_2O_3}$.

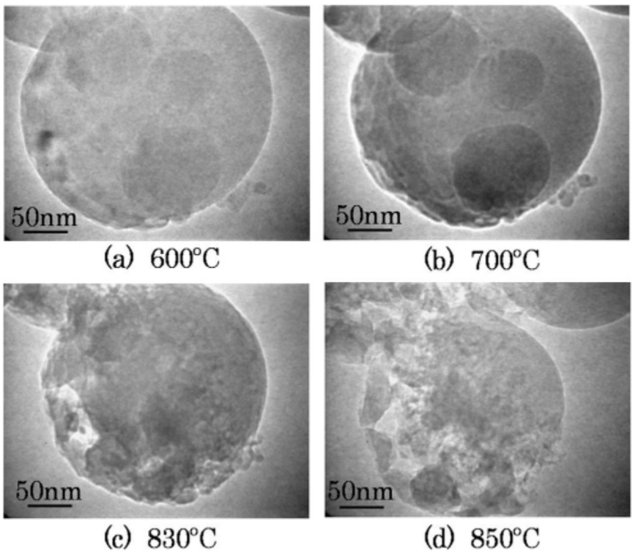

Fig. 4. Video image of the alteration process of SiO_2 grain. After heating at high temperature, the spherical SiO_2 grains changed drastically.

grains were concluded to be amorphous silica (Morioka *et al*., 1998; Kamitsuji *et al*., 2003). The vacuum-deposited aluminum layer on the SiO_2 grain at room temperature is composed of Al crystallites with the diameter of 20 nm, as shown in Fig. 2(a). The dark spots on a spherical surface are Al crystallites. By heating the sample at above 400°C in vacuum, these crystallites become larger by grain growth. Upon heating at 600°C, the Al crystallite on the surface of the SiO_2 grain becomes a uniform film, as shown in Fig. 2(b). The electron diffraction (ED) pattern showed that most of the crystal was Al.

Figure 3 shows the high-resolution transmission electron microscope (HRTEM) image of the interface between the Al layer and SiO_2 grain heated at 600°C. Lattice images of Al and γ-Al_2O_3 are seen in the Al layer. The Moiré fringes of 0.574 nm are due to $(111)_{Al}$ and $(222)_{\gamma\text{-}Al_2O_3}$ with the rotation of 23°. Therefore, 10 nm-diameter γ-Al_2O_3 particles were produced at the interfaces between Al and SiO_2 grains. This indicates that γ-Al_2O_3 was produced by the diffusion of oxygen atoms from SiO_2 to the Al layer, i.e., a reaction between Al and SiO_2 took place. The growth of Al_2O_3 crystallites in the Al layer implies void formation in the SiO_2 grain.

The samples were directly heated at above 600°C in the TEM with the special holder that can heat the sample to 1500°C in the vacuum (10^{-6} Pa) environment of the TEM (Kimura *et al*., 2000). The alteration process of the same grain was captured as video images, as shown in Fig. 4. Since the melting point of Al is 660°C, the surface Al layer completely covered the entire surface of the SiO_2 grain. As the reaction rate between Al and SiO_2 increased, the γ-Al_2O_3 phase was also formed on the opposite side of SiO_2 where no Al layer was initially deposited. A typical example of the specimen heated at 750°C is shown in Fig. 5. The black spots are the γ-Al_2O_3 crystals, as is shown in Fig. 5(b). This means that the Al layer was also changed into the corundum phase by the diffusion of oxygen from the SiO_2 grain. Upon increasing the heating temperature to above 800°C, the ED pattern showed that the surface Al layer was altered to δ-Al_2O_3 from γ-Al_2O_3. The formation of void clusters in the SiO_2 grain region was increased, as is shown in Figs. 4(c) and (d). The surface Al was fully changed to δ-Al_2O_3. Because of the formation of corundum on the surface of the SiO_2 grain, vacancies and clusters of vacancies were formed in the SiO_2 grain. In addition to the increase of vacancies, the SiO_2 grain became silicon rich, i.e., the SiO_x phase was formed. As indicated in a previous

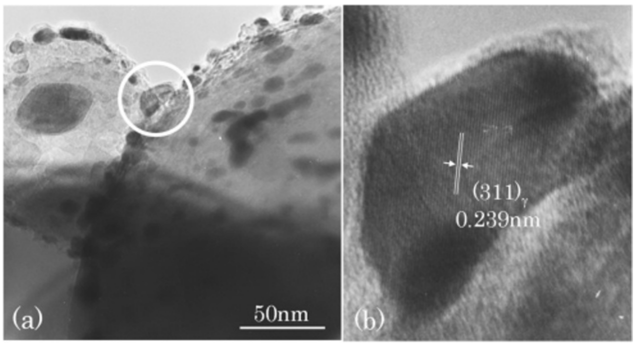

Fig. 5. TEM images of the SiO_2 grain surface covered with Al layer after heating for 20 min at 750°C. (a) SiO_2 surface of the opposite side. (b) HRTEM image of area indicated by a circle in (a). Growth of γ-Al_2O_3 crystallite is clearly seen.

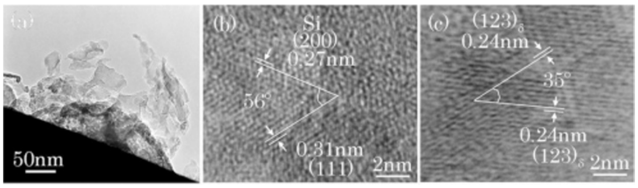

Fig. 6. TEM images of the specimen after cooling. The original shape of SiO_2 is lost. The crystal of δ-Al_2O_3 and small crystallite of silicon remain as shown in (b) and (c).

paper, SiO_x grains composed of silicon and SiO_2 crystallites evaporated above 800°C upon the formation of the SiO phase (Kamitsuji *et al.*, 2004). In the present specimen, the SiO_2 grains also evaporated, as is indicated in Figs. 4(c) and (d). The SiO_2 grains lose their shape, as shown in Fig. 6(a), after heat treatment. The ED pattern indicated δ-Al_2O_3, which is the phase produced above 840°C (Kimura *et al.*, 1996). The shape of the grain is lost. The HRTEM images of these altered grains are shown in Figs. 6(b) and (c). In addition to δ-Al_2O_3 crystals, which are identified on the basis of the closed lattice image distance and angles, small silicon crystals can be seen. This indicates that the reduced SiO_2 grains were changed into $Si+SiO_2$. As was elucidated by the heating experiment of SiO, the Si crystallite grew predominantly at 400 to 600°C during the heating and cooling periods (Morioka *et al.*, 1998). In the present experiment, the Al-mantle SiO_2-core grain can be easily changed to Al_2O_3 and silicon crystallites. The vaporization of SiO accompanying the growth of Al_2O_3 occurred. Although SiO_2 is one of the stable phases in siliceous dust, the above alteration upon the formation of the aluminium phase may have taken place in the siliceous dust via the heterogeneous nucleation of metallic aluminium. The present Al-mantle silicate-dust-core grains may be easily produced in interstellar medium. The thermal sputtering due to shock waves causes the dust to be immersed in high-temperature gas. Therefore the alteration of silicate dust may occur.

4. Summary

Vacuum-deposited Al on an amorphous SiO_2 grain of spherical shape was heated in vacuum. The in-situ observation of the formation process of Al_2O_3 was accomplished. Al_2O_3 formation on the surface of the SiO_2 grain took place above 750°C. The formation of Al_2O_3 caused the composition of the SiO_2 grain to change to SiO_x. The evaporation of SiO_x took place above 800°C, i.e., the possibility of SiO_2 dust destruction was found. In the theoretical estimation of Al_2O_3-core silicate-mantle grains in O-rich AGB stars (Kozasa and Sogawa, 1997), Al and SiO gases are key species in the formation of the core-mantle structures. If the surviving Al gas is deposited onto solid silicate grains, the growth of Al_2O_3 takes place. Therefore the formation of the Al_2O_3 phase and remaining small SiO_2 silicate is possible through the present process.

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S. Sasaki, H. Suzuki, Y. Kimura, T. Sato, T. Tanigaki, O. Kido, K. Kamitsuji, M. Kurumada, and C. Kaito (e-mail: kaito@se.ritsumei.ac.jp)