A&A 422, 975–979 (2004)
DOI: 10.1051/0004-6361:20034353


Astronomy & Astrophysics

# Direct observation of the metamorphism of silicon oxide grains

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Received 19 September 2003 / Accepted 23 March 2004

**Abstract.** Experimental studies on the metamorphism of $SiO_x$ grains under heating at $10^{-6}$ Pa have been conducted using a high-resolution transmission electron microscope. Si crystallites were predominantly grown at 500 to 700 °C in $SiO_x$ grains. The Si crystallites disappeared at 800 °C and evaporated as the SiO phase.

**Key words.** astrochemistry – acceleration of particles – method: laboratory – Stars: AGB and post-AGB – stars: circumstellar matter – ISM: dust, extinction

## 1. Introduction

Dust formation in oxygen-rich ejecta is based on excess oxygen and the elements Mg, Fe, Si and Al. Therefore we expect the formation of silicates and other metal oxides. This expectation is confirmed by spectroscopic observations of circumstellar envelopes around M-type giants (Dorschner & Henning 1995; Henning et al. 1997; Sandford 1996). The formation of silicates should start with the formation of $SiO_x$ clusters. Laboratory experiments with $H_2$-SiO-FeO-SiO, and $H_2$-Mg-SiO systems suggest the formation of amorphous unequilibrated solids with non-stoichiometric element ratios (Nuth 1996). The detection by ISO of a crystalline silicate component in the spectra of evolved stars has awaited a detailed explanation (Waters et al. 1996). We previously demonstrated the production of crystalline forsterite grains due to the coalescence and growth of Mg and SiO smoke grains (Kaito et al. 2003). The High-Resolution Transmission Electron Microscope (HRTEM) shows that the SiO film produced by vacuum condensation following the evaporation of SiO powder is composed of a mixture of silicon and $\alpha$-cristobalite nanocrystallites (Kaito & Shimizu 1984). The shift of infrared peaks that occurs when the film is heated in air has been understood as a phase transition of $SiO_2$ into an amorphous state with accompanying oxidation of silicon metal nanocrystallites (Morioka et al. 1998). The initial film was completely changed into a quartz film upon heating at 500 °C. Similar experiments using SiO grains prepared by the evaporation of SiO powder in an Ar gas atmosphere (gas evaporation technique) yield the same results for the film (Morioka et al. 1997). The metamorphic alteration in the amorphous state can be duplicated in the solid state in air.

Since the estimated pressure of the solar nebula at 2–3 AU is low (Nagahara et al. 1994), experiments on metamorphism in a vacuum are important for comparison with condensation, evaporation, melting and crystallization in the primitive solar nebula (Nuth 1996; Mysen & Kushiro 1988). We can directly observe phenomena involving any grains at high temperature by using the special heating holder attached to a transmission electron microscope (TEM). In a recent experiment, we succeeded in observing new phenomena such as the temperature dependence of dissolution and the precipitation of carbon on SiC grains using HRTEM (Atou et al. 2003; Kimura et al. 2003).

In this paper, we report direct observations of the heating of $SiO_x$ grains up to 1000 °C in vacuum at $10^{-6}$ Pa. The dynamic behavior of the grains was recorded on video tape.

## 2. The experiments

$SiO_x$ grains were produced by evaporating commercial SiO powder in Ar gas at 10 kPa (Morioka et al. 1997). Yellowish grains of $SiO_x$ (including $Si_2O_3$) were collected on glass plates (Phillips 1971). The collected samples were placed in the sample holder used for in situ observation of the heating process (Kimura et al. 2003).

Metamorphism of the specimen was directly observed using a Hitachi H-9000NAR HRTEM with a special heating holder, which can be heated to approximately 1500 °C (Kimura et al. 2000). The images were magnified by a factor of twenty using a television system. The images were recorded on video tape.

## 3. Results and discussion

As-grown SiO grains collected on a standard electron microscopic grid are shown in Fig. 1a. Spherical particles of 30 nm in diameter were produced. As indicated by arrows, small black dots ~2 nm in size can be seen in each particle. Electron diffraction (ED) patterns showed that the grains produced were amorphous.

The HRTEM image of part of a grain is shown in Fig. 1b. As indicated by arrows, lattice fringes can be seen in the range

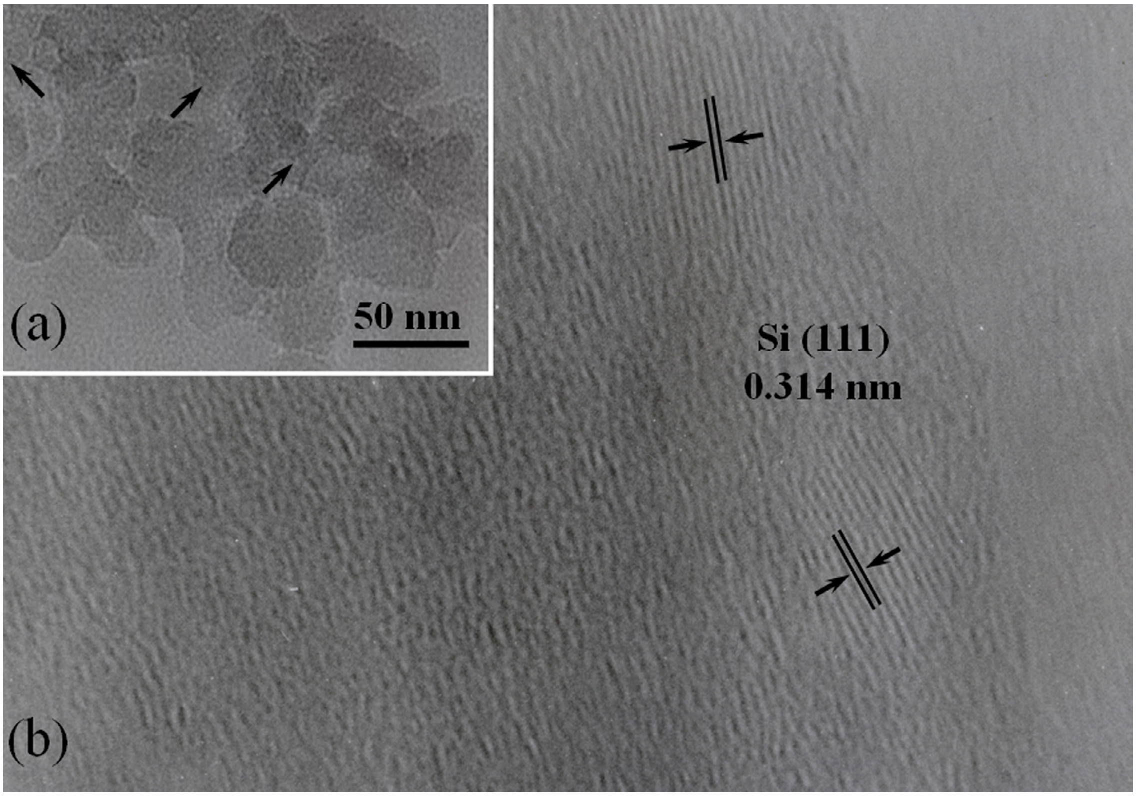


**Fig. 1.** TEM image of a SiO grain. Si crystallites can be seen as black dots as indicated by arrows in the low-magnification image. These black dots correspond to Si crystallites as seen in the high-resolution image in this photograph.

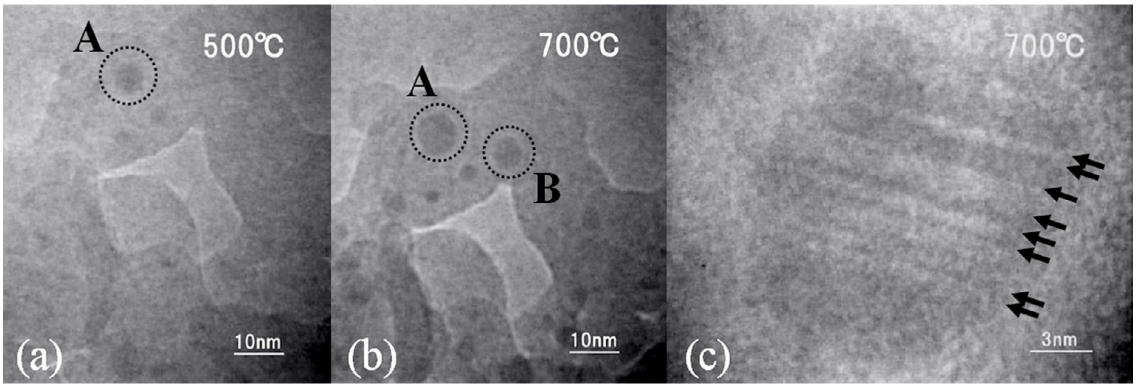


**Fig. 2.** In situ image of heated grains at **a)** 500 and **b)** 700 °C. The black region is due to the growth of silicon crystallites between 500 to 700 °C. Typical stacking faults of Si metal in an SiO particle are shown in **c)**.

of 2 nm and thus the black dots are identified as silicon metal crystallites. The IR spectrum of these particles showed the characteristic $\beta$-cristobalite spectrum (Morioka et al. 1997). Therefore, the SiO grains we started with were composed of silicon metal and $\beta$-cristobalite ($SiO_2$) as described in a previous report on the basis of spectroscopy (Morioka et al. 1997). In the present HRTEM observation of the grains, the existence of metallic silicon was also confirmed as was the film (Kaito & Shimizu 1984).

### *3.1. Metamorphism of $SiO_x$ grains in a vacuum*

When heating the $SiO_x$ sample at 450 °C in a vacuum, no significant structural alterations were observed. Upon heating at 500 to 700 °C, silicon crystallites, indicated in Fig. 1b, grew in the $SiO_x$ grains. Figures 2a and 2b show the TEM images printed from the video image of $SiO_x$ particles at the same place at 500 and 700 °C. The area of black contrast indicated by circle A in Fig. 2b was larger than that in Fig. 4a. A new, large, black-contrast area was seen in circle B. In another region, the black contrast area became larger upon heating at 700 °C. Silicon metal crystallites became predominant at 700 °C. The enlarged image in Fig. 2c shows stacking faults in a grown silicon crystal. This silicon crystal growth suggests that Si atoms diffuse in $SiO_x$ between 500 to 700 °C.

Figure 3 shows the ED patterns from grains heated to 500, 750 and 1000 °C. The haloes become sharp in spite of the

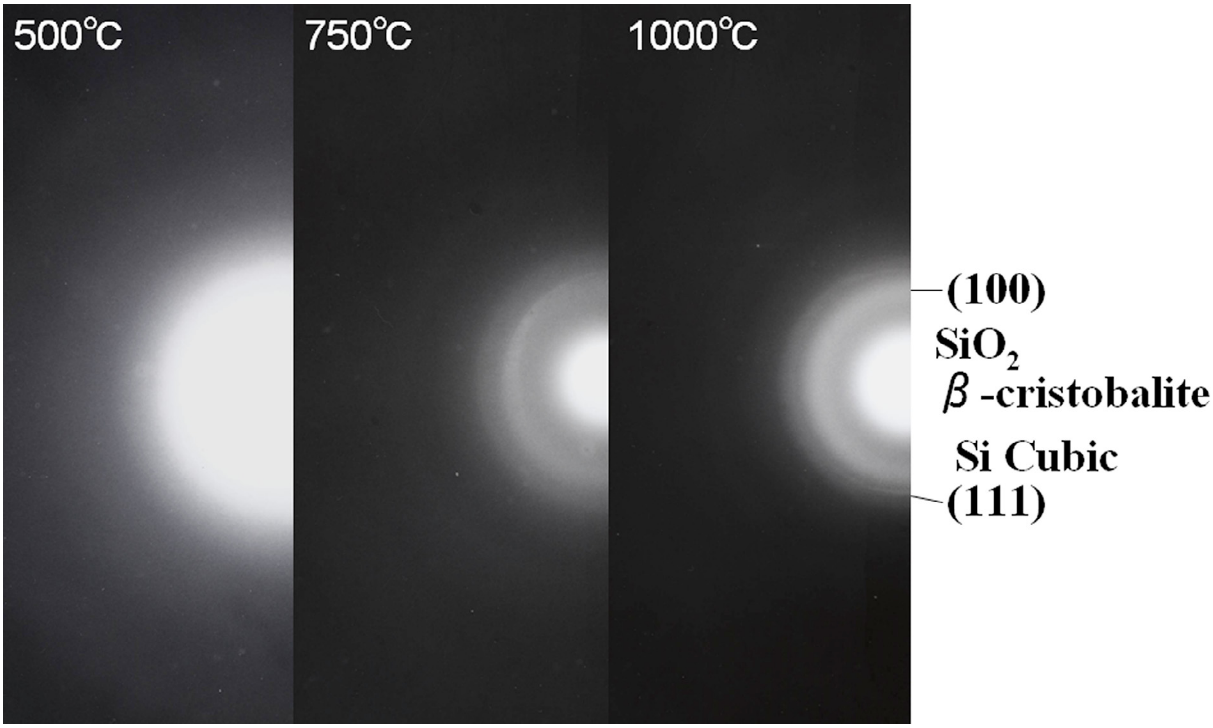


**Fig. 3.** Typical ED patterns in SiO grains at 500, 750 and 1000 °C respectively. Diffuse rings became sharper in spite of the high temperature. The diffraction rings can be identified as those of Si and $\beta$-cristobalite.

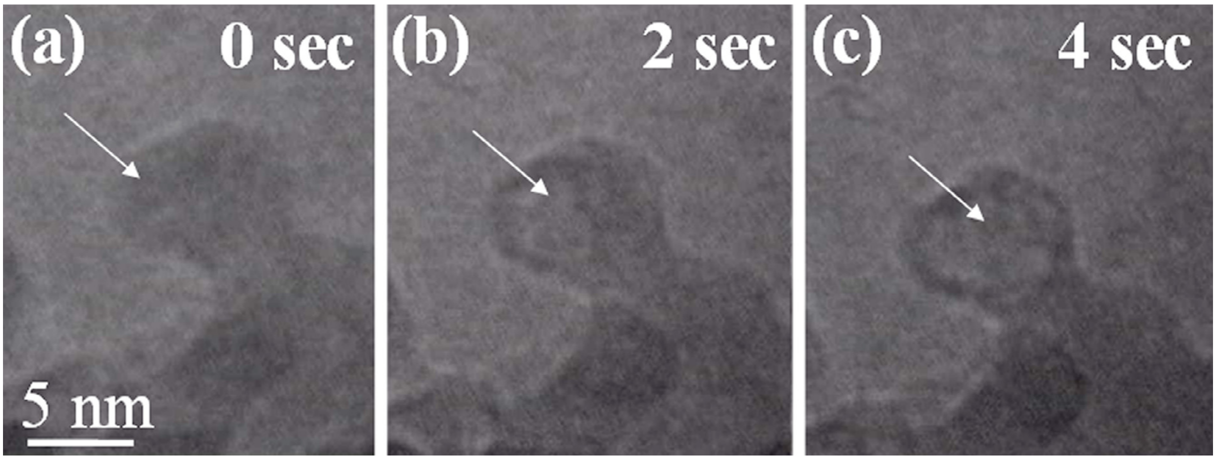


**Fig. 4.** Evaporation of an SiO particle heated at 900 °C. The Si crystallite seen in Fig. 4 disappeared and evaporation began. The SiO phase was formed and began to sublime. Figures 4a–c show the same particles. The time intervals from **a)** to **b)** and **a)** to **c)** are 2 and 4 s, respectively.

heating. It also becomes evident from the ED pattern that Si and $SiO_2$ crystallites grow in $SiO_x$ grains.

Upon heating to 900 °C, the silicon metal crystals seen as the black contrast areas became smaller and finally disappeared. As shown in Figs. 4a–c, parts of the grains indicated by arrows gradually evaporated. The evaporation rate was ~3 nm/s, as estimated from the video images at 900 °C.

The solid grains and films of $SiO_x$ were composed of a mixture of $SiO_2$ and Si. Up to 700 °C the silicon crystallites grew, and they disappeared when evaporation occurred above 900 °C. This shows that SiO component grains form at high temperature in agreement with the phase diagram of the Si-$SiO_2$ system (Sosmamn 1995). However, the present SiO formation temperature is about 75% lower than bulk data would indicate. These effects are similar to those observed in grain formation by coalescence in the Mg-SiO smoke system at low temperature (Kaito et al. 2003). Since SiO smoke can be obtained by evaporation of SiO powder from a tungsten boat by heating above 1400 °C, the evaporation seen in Fig. 4 occurs at temperatures ~60–70% lower.

When the grains were cooled down, silicon metal crystal growth could again be seen to occur predominantly in the range of 750 to 500 °C. A typical TEM image and corresponding ED pattern of the specimens cooled to 700 °C are shown in Fig. 5. The diffraction rings can be interpreted as showing the existence of silicon metal crystals of about 10 nm in

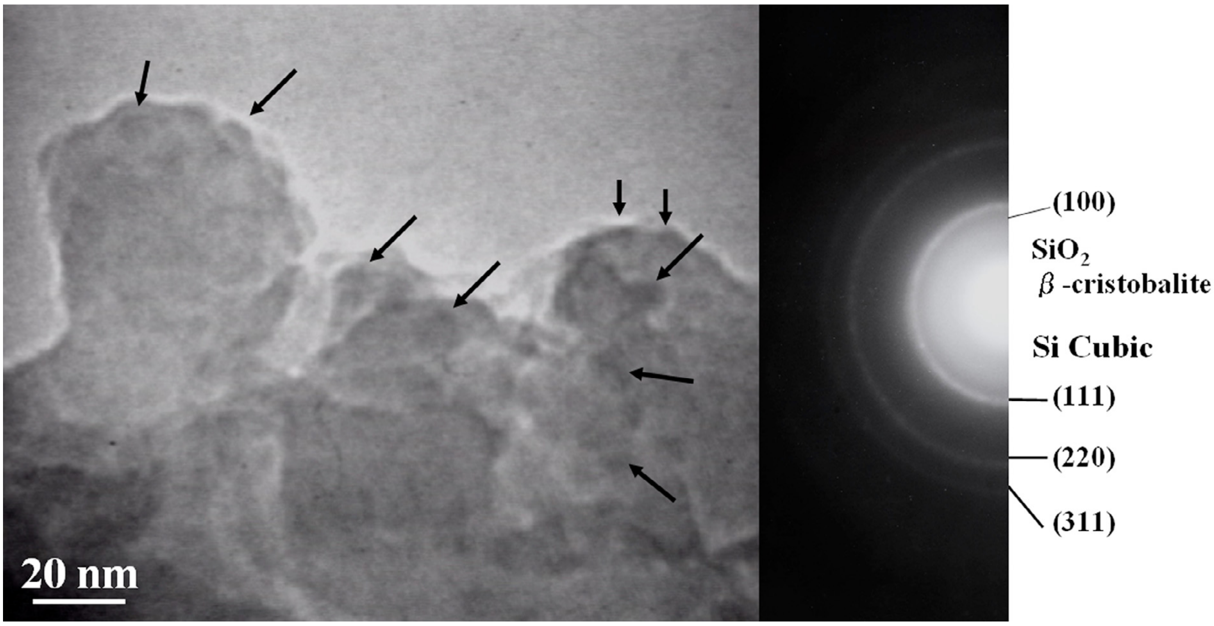


**Fig. 5.** When the SiO grains are cooled to 700 °C, the appearance of silicon crystallites was seen as indicated by arrows. This is also consistent with the result of heating the specimen as indicated in Fig. 2. The ED pattern clearly shows the growth of silicon crystallites.

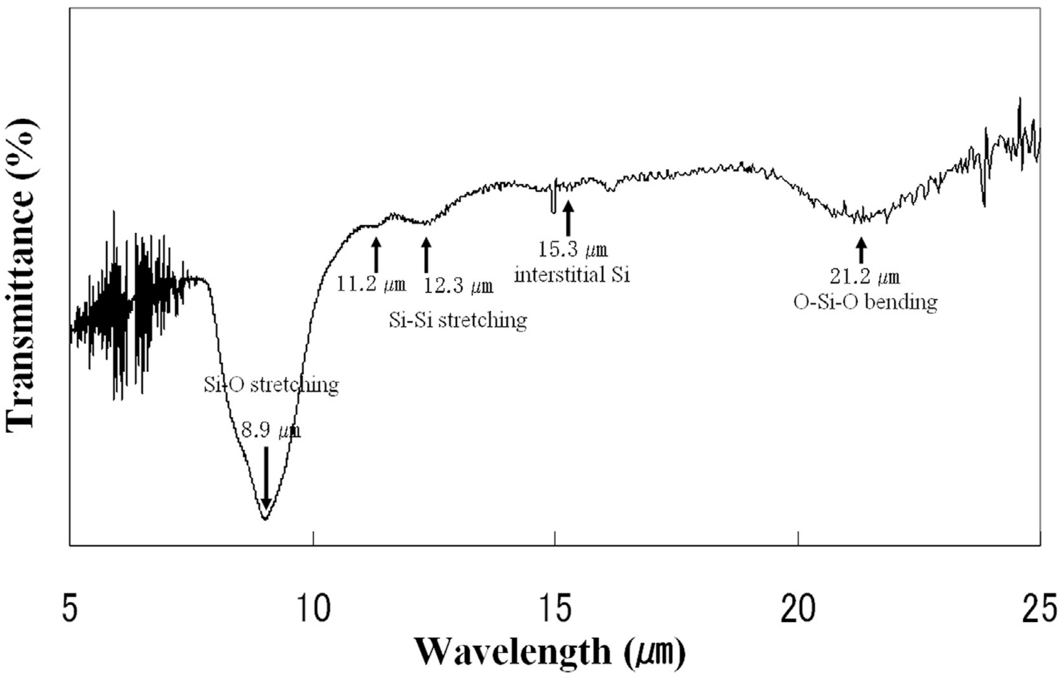


**Fig. 6.** IR spectrum after heating the SiO specimen at 750 °C. Characteristic Si-O stretching at 11.2 and 12.3 $\mu$m due to $\beta$-cristobalite can be clearly seen.

diameter. IR spectra before and after heat treatment in vacuum did not change, since silicon metal is not IR active. Figure 6 shows the IR spectra of the $SiO_x$ grains after heat treatment at 750 °C. The characteristic absorption indicates the existence of $\beta$-cristobalite (Morioka 1997).

The SiO phase can be obtained by heating $SiO_x$ grains above 800 °C in a vacuum. The selective growth of silicon nanocrystals took place between 500 and 750 °C. The as-grown $SiO_x$ grains produced by gas evaporation were composed of silicon metal and $\beta$-cristobalite in contrast to the as-deposited film, which was composed of silicon and $\alpha$-cristobalite (Kaito & Shimizu 1984; Morioka et al. 1998). This is due to the difference in condensation from the gas to solid, i.e., $SiO_x$ grains in this experiment were condensed near the evaporation source and kept at about 500 °C at 5 nm above the evaporation source (Kaito & Fujita 1986); therefore, silicon crystallites were grown and the high-temperature $\beta$-phase was retained after cooling below 500 °C. In the case of film growth, the more

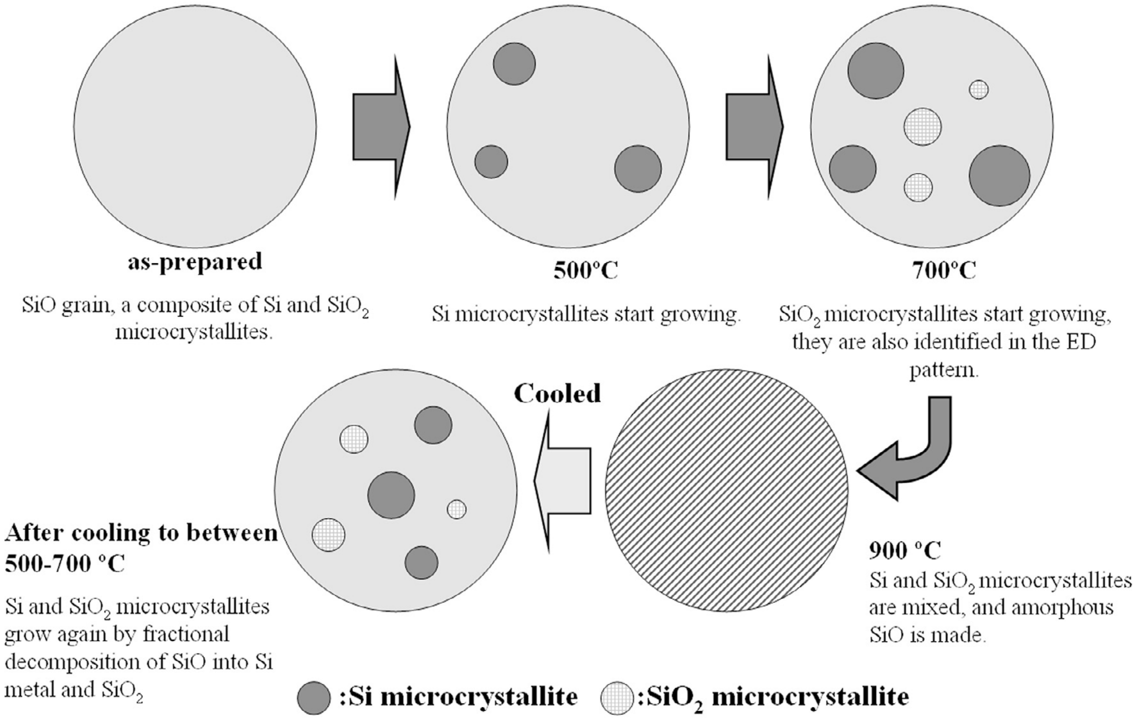


**Fig. 7.** Schematic picture of the decomposition process of a particle.

rapid condensation from the vapor phase onto the relatively cool substrate is dominant (Morioka et al. 1998); therefore, a metastable phase is produced (Rietmeijer et al. 1999).

## 4. Conclusions

Partial evaporation of $SiO_x$ grains, composed of Si and $SiO_2$ crystallites, is due to the formation of the SiO phase during vacuum heating. The main changes in the SiO grains caused by heating are summarized schematically in Fig. 7.

Since silicate dust has been detected in different objects, such as in the circumstellar envelopes of evolved stars, planetary nebula, young stellar objects, proto-planetary disks and comets, it is likely that many grains have undergone some degree of metamorphism since their formation (Nuth 1996). In the present experiment on $SiO_x$ grains, it is evident that the formation of $SiO_x$ grains and the evaporation of the SiO phase took place at about 70% lower temperature than one would expect from the bulk data. Though from the thermodynamic data the vapor pressure of SiO at 900 °C was estimated to be of the order of $10^{-3}$ Torr (Nuth & Donn 1982), the contribution of surface energy can accelerate the evaporation of grains. A similar effect can be seen in the process of coalescence and growth in the smoke (Kaito 1985). The crystalline forsterite grain formation by coalescence between Mg and SiO grains at a few hundred degrees centigrade in space is also due to the characteristic behavior of nanometer-scale grains as illustrated by the behavior of the present SiO grains. Since dust formation in oxygen-rich stars is based on excess oxygen and the elements Mg, Fe, Si and Al, the dynamic behavior of metallic clusters and oxide grains may also become important in the metamorphism of grains. If $SiO_x$ grains exist in the excess oxygen gas at a few hundred degrees centigrade, then the grains may oxidize to $SiO_2$ grains (Morioka et al. 1997). The direct alteration of these $SiO_2$ and $SiO_x$ grains due to their reaction with deposited metal clusters is now being studied experimentally. Some results may be reported in the near future.

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