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Magnesiothermic reduction of silica glass substrate—Chemical states of silicon in the generated layers

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ABSTRACT

We applied magnesiothermic reduction to silica glass substrates at various conditions including solid state or solid-Mg liquid reaction, and solid-Mg vapor reaction. Magnesium silicide with highly oriented to the ⟨110⟩ direction against the substrate surface was obtained in the solid state reaction at temperatures from 600 °C to 700 °C using Mg grains while Si crystallites were obtained in the reaction with Mg film deposited on the glass substrate at 560 °C. On the other hand, in the reduction with Mg vapor at 575 °C, brown and amorphous layer was formed on the surface of the silica glass substrate. The layer was transparent in the visible and near-infrared regions, and showed an interference pattern in the transmission spectra, indicating the homogeneity of the layer. The thickness and refractive index were estimated as 770 nm and 1.94, respectively. As the reaction with Mg vapor proceeded further, Mg_2Si and MgO crystallites were formed. Oxidation states and their depth profiles of silicon atoms in the layers were investigated by X-ray photoelectron spectroscopy. The silicon atoms in the brown and amorphous layer existed in intermediate oxidation states, −2 and +3. The reaction proceeding, the formal charge of the silicon atoms varied to −4 corresponding to Mg_2Si and +2.

1. Introduction

In recent years, magnesiothermic reduction of various kinds of silicon dioxide with micro- to nano-structured morphology has received much attention [1–10]. Because this reaction proceeds at relatively low temperatures, approximately 600 °C–750 °C, the silicon dioxides are reduced to silicon retaining their original micro- and nano-structures. Bao et al. reported that silica diatom frustules could be converted to silicon replicas retaining the three-dimensional nanostructures of the original frustules with the magnesiothermic reduction at 650 °C [1,2]. Since the paper was published, this type of reaction has been carried out for various silicon dioxide nanocrystallites, such as mesoporous silica synthesized by polymer-templating methods [3], silica opals made of periodically-ordered silica microspheres [4], sea sands with nanopores [5], porous silica glasses [10] and fibers. Micro to nano-structured silicon prepared through this reaction is expected to have potential applications for anodic materials in Li ion batteries, sensors, light-emitting devices, catalytic materials, and so on. Furthermore, the magnesiothermic reduction was also applied to a glass substrate. An Mg-coated soda-lime silicate glass was heated at 520 °C and then washed with 1M HCl solution in order to remove the byproducts [11]. According to the authors, Raman spectra of the reacted glass showed a band at 520 cm^{-1} characteristic to silicon nanocrystallite.

On the other hand, Gutman et al. reported a reaction of silica glass and single crystal quartz with Mg powder at various temperatures ranging from 450 °C to 640 °C [12–14]. The total reaction written by the equation,

$$SiO_2 + 4Mg \rightarrow 2MgO + Mg_2Si, \quad (1)$$

occurred in this case. They found that a unique periodic layered structure composed of MgO-rich and Mg_2Si-rich phases was generated at the reaction interface. Thus their research attention has been focused on the formation mechanism of the periodic structure. In the literatures, however, generation of silicon crystallites was not explicitly mentioned. They also did not describe the silicon-related compounds with a silicon atoms in

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the intermediate oxidation states between silicon dioxide (+4) and silicon (0), or silicon and magnesium silicide (−4). Furthermore, Uchino et al. reported that nanocomposites consisting of insulator (MgO)/semiconductor (Mg_2Si)/superconductor (MgB_2) were obtained through the magnesiothermic reduction of a borosilicate glass using Mg powder and that the nanocomposites exhibited semiconductor-superconductor transition owing to the MgB_2. They closely investigated the interfacial atomic structure between the MgO-rich and Mg_2Si-rich phases [15].

In the present paper, we perform the magnesiothermic reduction for synthetic silica glass substrates in order to investigate the possibility to prepare silicon crystallites or silicon-related materials with high refractive index on the silica glass substrates. Silica glass is one of the key materials for photonic devices, and highly pure and transparent starting materials are easily available. Therefore, if silicon or silicon-related layers with optical quality are obtained on silica glass substrates by the magnesiothermic reduction, this is expected to be a potential rout for fabrication of devices with high-refractive-index contrast such as the silicon-on-insulators [16,17]. As another possible application, the magnesiothermic reduction of silica glass substrate is expected to be used for the fabrication of solar cell grade silicon [18,19].

Since magnesium silicide is thermodynamically the most stable compound in the reaction of silicon dioxide and magnesium [13], it is of importance to control the reaction to generate desired silicon or silicon-related compounds as a predominant product. For this purpose, we performed the reduction at various conditions, such as solid-state or solid-Mg liquid reaction, and solid-Mg vapor reaction. Silicon-related compounds are composed of silicon atoms in intermediate oxidation states, i.e., between +4 and 0, or 0 and −4 in the formal charge. Among them, nonstoichiometric SiO_x ($x < 2$) and stoichiometric SiO have received much attention, and the structure and electronic states have been research subject for practical application [20–26]. Thus, it is also interesting to clarify the relationship between the reaction conditions and the chemical states of silicon in the reaction products. In the present work, the chemical states of silicon and their distribution along the depth from the reaction surface were investigated by means of the X-ray photoelectron spectroscopy (XPS). We discuss the results from the viewpoint of the reaction mechanism between silica and magnesium including the thermodynamic aspect.

2. Experimental procedures

We performed the magnesiothermic reduction with two methods, one is the solid state or solid-liquid reaction of silica glass with magnesium, and the other is the reaction with magnesium vapor. These reaction setups are illustrated in Fig. 1. In the solid state or solid-liquid reaction, we tried two ways, in which synthetic silica glass substrates with approximately $5 \times 30\,mm^2$ in size and 2 mm in thickness were used. In one way as illustrated in Fig. 1(a), the silica glass substrates embedded in Mg grains were heat-treated. The silica substrate with Mg grains was put in a stainless tube of 3/8 in. in outer diameter under Ar atmosphere; the one side of the tube was sealed with a Swagelok® stainless cap. Then the other side of the tube was sealed with another stainless cap and the tube was heated at 600 °C, 650 °C, or 700 °C for three hours. Because the melting point of magnesium is 649 °C, at the latter temperature, magnesium is expected to be melted. The Mg grains were prepared from Mg tips by grinding and treating with 1.2M HCl solution to remove oxides from the surfaces before using. In the other way as illustrated in Fig. 1(b), magnesium was deposited on the silica glass substrate. The magnesium deposition on the substrate was performed in a vacuum deposition apparatus (ULVAC, VPC-60) with a base pressure less than 5×10^{-3} Pa. The thickness of the deposited Mg film was approximately 4.9 μm evaluated by a laser microscopy. The Mg-deposited silica glass substrate was put in a stainless tube of 3/8 in. in outer diameter and both sides of the tube were sealed with Swagelok® stainless caps under Ar atmosphere. The stainless tube was heated at 560 °C for three hours.

For the reaction with Mg vapor as illustrated in Fig. 1(c), we used synthetic silica disks of 7 mm in diameter and 1 mm in thickness, and Mg grains with less than 1 mm in size as vapor source. The Mg grains were prepared from Mg tips by the same method as mentioned above. The magnesium reduction was performed in a stainless steel tube of 3/8 in. in outer diameter with Swagelok® stainless caps. First, 1 g of Mg grains were put in the tube, a side of which was sealed with a cap, and then an inner pipe of stainless steel of 30 mm in length and 7 mm in outer diameter was put on the Mg grains. Subsequently, a silica glass disk was put on the inner pipe, and then the other side of the stainless tube was sealed with a cap. The inner pipe worked as a spacer to keep the distance between the magnesium and the silica disk constant, i.e., 30 mm. The setting

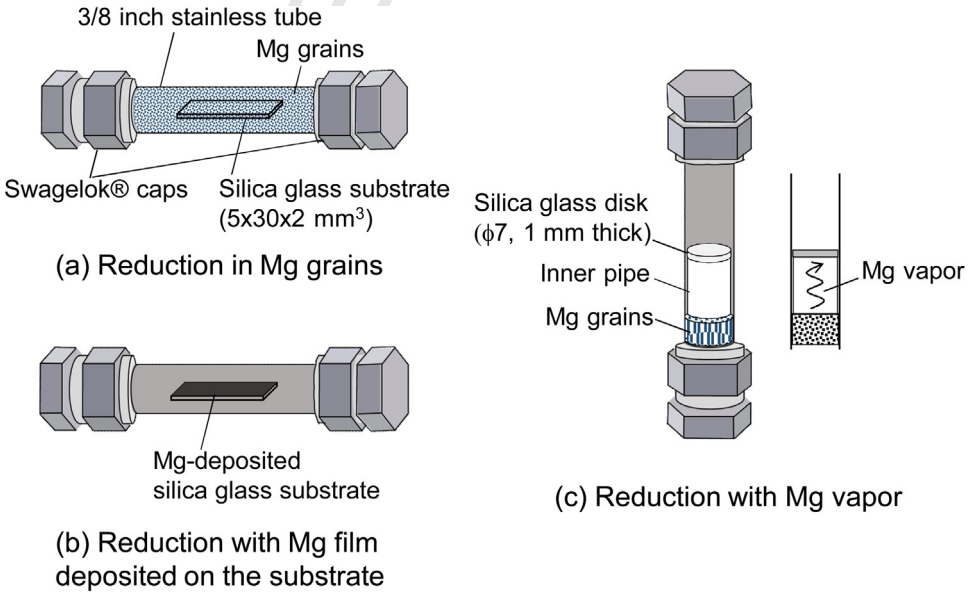

Fig. 1. Experimental setups for magnesiothermic reduction at various conditions. (a) Reduction in Mg grains, (b) reduction with Mg film deposited on the silica glass substrate, (c) reduction with Mg vapor. (a) and (b) are the solid state or solid–liquid reaction, and (c) is the solid–vapor reaction.

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