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Synthesis of platinum silicide at platinum/silicon oxide interface by photon irradiation

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ABSTRACT

The synthesis of platinum silicide at a Pt/SiO_x interface by photon irradiation was investigated using transmission electron microscopy. A platinum silicide, Pt_2Si, was successfully formed at the Pt/SiO_x interface by irradiation with 680 and 140 eV photons, but not by irradiation with 80 eV photons. Silicide formation was also induced by irradiation with electrons of energy 75 keV. The amount of silicide formed by photon irradiation was lower than the amount obtained by electron irradiation. Silicide formation by both photon and electron irradiation was accompanied by Si depletion in amorphous SiO_x. The experimental results indicate that silicide formation is induced by electronic excitation. A possible mechanism for silicide formation is proposed on the basis of the results.

1. Introduction

High-energy particle irradiation (i.e., ion and electron irradiation) is widely used and is one of the most effective tools for materials modification. Studies of this subject are of significance not only from the scientific point of view, for elucidation of the mechanisms behind the modifications, but also from the technological point of view, to achieve advanced functionalization of materials. If we confine ourselves to inorganic nonmetallic materials, examples of studies in this area are as follows: formation of amorphous Si with a controlled degree of crystallinity by co-irradiation with MeV electrons and MeV ions [1], recoil implantation of foreign atoms into semiconducting substrates by MeV electron irradiation [2], amorphization of crystalline Si by MeV electron irradiation [3], doping of impurity atoms into semiconductors by ion implantation [4], and defect formation in CeO_2 by irradiation with a few hundred MeV ions [5,6].

In general, materials modification by high-energy particle irradiation can be achieved by two different routes, namely atom displacement caused by the direct knock-on of primary particles, and processes caused by excitation of the electronic system. (The latter includes, in some cases, atom migration and/or atom displacement, in addition to modification of electronic states.) However, our understanding of electronic excitation effects in materials modification is still insufficient, in contrast to the current, deeper understanding of knock-on atom displacement. At present, it is therefore difficult to investigate the two contributions separately in detail. Consequently, it is of primary importance to improve our understanding of the effects of electronic excitation on materials modification.

In view of this background, research on whether or not a solid-state reaction can be controlled by excitation of the electronic system can be regarded as one of the most interesting research

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themes that touch the core of this subject. On the basis of this premise, two of the present authors (HY and HM) have been engaged in the study of solid-state reactions that do not occur under thermal annealing conditions (i.e., solid-state reactions for which the Gibbs free energy change, ΔG, is positive) but do occur in an electron excitation environment [7,8], with a focus on reactions induced by excitation of inner-shell electrons. To date, it has been found that (1) a compound semiconductor, GaSb, can be decomposed or dissociated to a mixture of Ga and Sb by low-energy electron irradiation, with no knock-on atom displacement [7], although ΔG for the decomposition reaction, $GaSb(s) \rightarrow Ga(s) + Sb(s)$, is positive, and that (2) a silicide, Pt_2Si, can be successfully synthesized at the Pt/SiO_x interface by similar electron irradiation [8], although ΔG for the silicide synthesis reaction is again positive [9]. Experimental results for silicide synthesis [8] suggest that dissociation of the substrate material, SiO_x, is first induced by electronic excitation and then one of the dissociation products (i.e., a Si atom) may react with neighboring Pt deposited on the substrate, resulting in the formation of a Pt_2Si layer at the Pt/SiO_x interface. Photochemical research on isolated molecules has established that there are examples of synthesis reactions in which fragmental species (mainly constituent atoms) produced by photoinduced dissociation reactions serve as one of the starting materials (or starting components) for the subsequent synthesis reaction [10]. However, to the best of our knowledge, no such examples have been reported in the field of solid-state reactions of inorganic materials.

It is therefore of interest to study whether or not the dissociation product (i.e., Si atoms) from the SiO_x substrate can actually serve as a starting material (or starting component) and participate in the subsequent reaction with the pre-existing Pt, eventually leading to silicide synthesis, using Pt/SiO_x composite samples. In the present study, to elucidate the mechanism behind the synthesis reaction, we used electromagnetic radiation (i.e., photon irradiation), with which energy-selective excitation of electrons can be achieved more accurately than with conventional electron irradiation, as, for example, in transmission electron microscopy. Based on these considerations, in this work, the synthesis of platinum silicide at the Pt/SiO_x interface, induced solely by photon irradiation, was investigated. The results confirmed that a silicide, Pt_2Si, can be successfully formed at the Pt/SiO_x interface by photon irradiation.

The authors believe that this work provides information that will contribute to a better understanding of electronic excitation effects in materials modification.

2. Experimental procedures

2.1. Sample preparation

Samples were prepared by two different methods. In the first method, Pt particles were grown almost epitaxially on (001)-cleaved NaCl substrates, kept at 573 K, by DC sputtering of a Pt target in a high-purity argon plasma (5 N purity). The argon pressure in operating mode was 8 Pa, and the applied voltage and duration were 370 V and 30–50 s, respectively. The particles were then backed with a supporting film, namely an amorphous SiO_x film of thickness approximately 20 nm, which was vapor deposited onto the Pt particles on the NaCl, after it had been cooled to room temperature. Lumps of silicon monoxide were used as the source. In the composite, Pt particles were embedded in one side of an amorphous SiO_x film [see Fig. S3(a) in the supplementary material (SM) for reference [8]], and Pt particles showed a strong preferred orientation along the [001] direction because of the epitaxial growth mentioned above. In the other method, amorphous SiO_x films of thickness approximately 20 nm were formed by vapor deposition on (001)-cleaved NaCl substrates kept at room temperature. Then Pt particles of size ~10 nm were formed on the oxide film at room temperature by DC sputtering of a Pt target under conditions similar to those used in the first method. The duration period was about 15 s. The orientation of grains in individual Pt particles was random, as can be seen from the continuous Debye–Scherrer rings in figures such as Fig. 6(b) and S1(b). In this paper, the Pt/SiO_x composite films prepared by the first and second methods are denoted by $Pt_{(epi)}/SiO_x$ and $Pt_{(poly)}/SiO_x$, respectively. Both types of Pt/SiO_x composite prepared on NaCl were then floated on distilled water and mounted on copper grids with a single hole of 0.3 mm^{φ} in their center for photon irradiation experiments and subsequent transmission electron microscopy (TEM) observations. The O content, x, in the SiO_x film was evaluated by X-ray photoelectron spectroscopy to be approximately 1.5 [8].

2.2. Photon irradiation experiments and TEM analysis

The Pt/SiO_x composite films on copper grids were irradiated with photons of energies 680, 140, and 80 eV with beam line BL13 in the Saga Light Source. The diameter of the photon beam was approximately 0.1 mm, and the photon fluxes were estimated to be around 1.8×10^{20}, 5.1×10^{21}, and 3.7×10^{21} photons/(m^2 s) for 680, 140, and 80 eV photons, respectively. The flux usually decreased by about 30% after irradiation for 14.4 ks. The irradiation temperature was room temperature. The copper grid, with the central 0.3 mm^{φ} hole covered with the sample film, was mounted on a holder in the beam line, and the grid position was carefully adjusted by accurately shifting the holder to allow the 0.1 mm^{φ} photon beam to pass through the hole almost at its center. This careful adjustment was made by monitoring the intensity of the photoelectron emission from the copper, i.e., by identifying the grid position at which there was no emission from copper. This enabled the photon beam to irradiate the sample film at around the center of the 0.3 mm^{φ} hole. These experimental procedures were necessary for subsequent TEM observations of the irradiated sample film, i.e., to enable ex situ, post photon-irradiation TEM studies of the sample. In irradiation of both the Pt (poly)/SiO_x and Pt (epi)/SiO_x composites, the sample was aligned so that the photon beam was always incident to the Pt side (i.e., incident to the other side of the SiO_x film) of the target sample.

In the TEM studies, bright-field images (BFIs), the corresponding selected area electron diffraction (SAED) patterns, and high-resolution electron microscopy (HREM) images were obtained. The electron microscopes used were a 100 kV microscope (Hitachi H7000) operated at 75 kV and 200 kV microscopes (JEOL JEM-ARM200F) operated at 200 kV.

Note that, as a reference, a series of electron irradiation experiments on the same samples were also conducted (see section 3.4).

3. Results and discussion

3.1. Formation of platinum silicide by irradiation with 680 eV photons

Fig. 1 shows an example of silicide formation in the $Pt_{(epi)}/SiO_x$ composite induced by 680 eV photon irradiation for 14.4 ks. Fig. 1(a)–(b) show a BFI of the composite before irradiation and the corresponding SAED pattern, respectively. Fig. 1(a) shows Pt particles of size approximately 10–20 nm, in most cases connected to each other, embedded in an amorphous SiO_x film. The SAED pattern in Fig. 1(b) can be consistently indexed to the [001] diffraction pattern of [001]-oriented face-centered cubic (fcc) Pt particles superposed on the Debye–Scherrer ring pattern of randomly oriented