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Comparison of silicon nanocrystals size determination by Raman scattering and transmission electron microscopy measurements

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Abstract

In the context of silicon nanoaggregates elaboration we have studied the Al–SiO_2 interface at temperatures under or above the eutectic point. We have reported the formation of diffusion limited aggregates (DLA) or deposition diffusion aggregates (DDA) of silicon. Raman scattering and X-ray analysis have proved the presence of crystalline silicon in these fractal structure and lead us to a typical elementary size in the nanometer range. TEM measurements confirm here the crystallite size and give informations on the silicon structure in high resolution mode. The reaction of Al on SiO_2 seems to be a good way to form silicon nanocrystals in SiO_2 matrix of calibrate size.

Keywords: Nanocrystalline silicon; Fractals; DLA; DDA; Raman scattering; TEM measurements

1. Introduction

We have reported previously by in situ measurements that small crystallisations appeared during annealing of the Al/SiO_2 interface [1,2] above approximately 500 °C with quite uneven distributions and lead to the formation of fractal structure depending of the temperature. These interface has a big interest in both the field of electronic component and of composite materials [3–7] and more recently in the silicon based opto electronics [21]. We have previously revisited the crystallisations in the context of fractal growth. The introduction of the diffusion limited aggregation (DLA) [8–12] and of the deposition diffusion aggregation (DDA) models [13–16] have helped us to understand the morphologies linked to diffusion limited growth. From the morphological point of view, the DLA type of aggregates has a highly ramified structure whereas the DDA type structure is much denser, with a rough or ragged contour.

Through X-ray analysis and Raman scattering measurements we have proved that these fractal structure are nanocrystalline silicon made. The broadening and the shift of the Si line have allowed us to conclude to a typical elementary size of the structure in the nanometer range.

The main purpose of this paper is to compare the size previously obtained by Raman scattering by the broadening and the shift of the Si line and TEM measurements in the high resolution mode. We want to confirm that the typical elementary size of the structure is in the nanometer range and they are silicon made.

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2. Experimental

We have designed an experimental set-up allowing to study in situ the annealing of Al thin films (2000A) on silica slides. This set-up is composed of a resistive coil located under a quartz sample holder allowing transmission illumination through the coil center (Fig. 1). The temperature is regulated through an Eurotherm regulator with an accuracy of one tenth of a degree. A probe linked to a thermocouple monitors the temperature inside the furnace and near the sample. The sample holder is introduced into the brass furnace equipped with nitrogen entries as well as branch pipes for the measurement of the material resistivity. The upper window of the furnace is also made of quartz so as to allow in situ acquisition of the sample images during annealing. The camera is placed above a tube. The images are recorded in real time, and processed at a later stage.

2.1. Morphological aspects

As shown in Fig. 2 a critical temperature T_c (577 °C) exists at which the creation of a liquid phase can be expected. We have effectively recently shown by in situ studies that the Al/SiO_2 reaction indeed leads to the formation of two structural types DLA (Fig. 3A) or DDA (Fig. 3B) whether we are in a quenching régime (very far from equilibrium, aggregation of the Si into DLA clusters) or in a temperature plateau (hence a constant flux of the Si produced by the reaction, which aggregates into DDA clusters). Also, different patterns are observed whether the reaction finds itself below or above the eutectic temperature of the Al–SiO_2 reaction [15,16]. Above the eutectic point, DLA-like filaments are obtained, which surround liquid drops of Al. From the morphological point of view, the DLA type of aggregates has a highly ramified structure with whereas the DDA type structure is much denser, with a rough or ragged contour. The difference is basically linked to the presence of higher diffusion gradients and a lower surface coverage in the case of DLA [6–10]. In DLA, particles diffuse and aggregate at nucleation centers. There is no source of diffusing particles other than the initial concentration of random walkers, which is progressively depleted as they deposit. In DDA, there is an external source of particles, generally constant, which showers the surface where nucleation and growth occurs. In our instance, the diffusing particles are the Si atoms which are produced by the thermal treatment. The Si clusters into small crystallites.

2.1.1. Below T_c

When the temperature is lower than the eutectic point, the reaction may last up to a few hours. During the plateau, and after an induction period, silicon-rich domains are formed (Fig. 4A–C), whose size increase with time (Fig. 4A and B). They appear as transparent clusters in transmission illumination (Fig. 4C) surrounded by a hot film. It is not wise to let the sample react thoroughly, for the DDA clusters eventually coalesce and the sample is fully reacted which makes it obviously impossible to observe these DDA type structures. The induction time is ascribed to the gradual increase of silicon concentration, until the Si concentration finds itself in supersaturation above the limiting concentration of the AlSi alloy in the solid states.

It is assumed that the temperature field is locally uniform. The driving force for aggregation is the low diffusivity of Si in Al, and the concentration gradients around the clusters. Thermal diffusivities, especially in the metallic phase, are classically two order of magnitude larger than elemental diffusivities. Moreover, the set-up is quite different from directional solidification, in that the boundary condition for temperature is a coil surrounding the area of interest. During the temperature plateau, there is a constant reaction rate at the Al/SiO_2 interface. This reaction

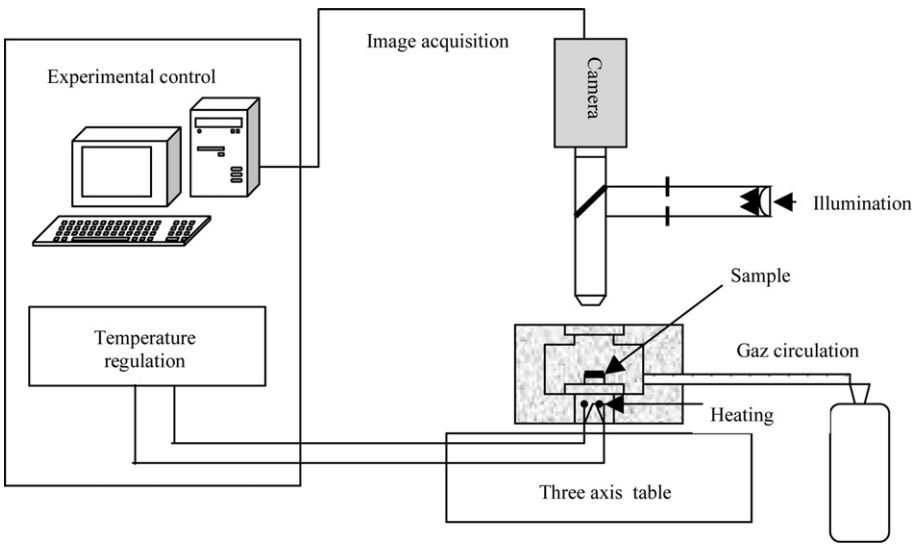

Fig. 1. Annealing is obtained by a torus placed under the sample. An infrared filter allows to visualize the aggregate growth.