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Sol-gel synthesis of Ge nanophases in silica

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Abstract

Elemental Ge nanophases are obtained in silica starting from a sol-gel synthesis. The process comprises the preparation of silica xerogel doped by Ge(IV), substituting for Si(IV) in the oxide network, followed by reduction and phase separation during the sintering process by reaction with H_2 or CO. X-ray diffraction, Raman spectroscopy and high resolution transmission electron microscopy show that reactions with H_2 give rise in the porous silica network to nanometer-sized crystallization of elemental cubic germanium. © 2007 Elsevier Ltd. All rights reserved.

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1. Introduction

Semiconductor quantum dots (OD) in silica are extensively investigated in several fields, particularly for photonic devices and electroluminescent materials [1]. In this field many works have been carried out on direct and indirect bandgap semiconductors [1-4]. In the case of Si nanostructures, the QD-size control, down to strong quantum confinement conditions, enables band-to-band radiative processes, usually not allowed in macroscopic crystalline systems [5]. Quantum confined Ge nanostructures have been studied as well, grown by vapour phase deposition or by epitaxy on ultraclean silicon surface [6,7] or by phase separation in heavily oxygen understoichiometric silica-germania sputtered thin layers [8]. By contrast, production strategies based on sol-gel synthesis have not been investigated up to now, even though they might be valuable to produce Ge nanostructures in silica by simple, versatile and environmentally safe chemical methods. Sol-gel chemistry indeed satisfies such requirements and in principle

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should enable us to obtain both bulk samples and thin films easily integrated on silicon substrates [9]. In this regard, few strategies may be considered to produce nanostructures embedded in silica.

A simple approach involves a cogelation procedure of presynthesized nanostructures in silica. This strategy is useful with nanostructures very different from oxide materials, like carbon nanostructures, sulphides, selenides, or metal colloids [10]. Main drawback is that such composite materials cannot be thermally treated at high temperature to remove organic contaminants or, even more difficult, to get a densified structure.

An alternative method induces the growth of nanostructures by phase separation from the silica matrix during high temperature thermal treatments [11]. The process is suitable for the production of a fully densified glassy material, but the chemical-physical process has to be strictly designed on the matrix chemistry. Model examples of such a process are TiO_2 and SnO_2 in silica, as well as sulphides and selenides in mixed glass. In these systems nanostructure formation is driven by the low solubility of the semiconductor phase in the matrix. However, nanosegregation of elemental semiconductors in silica, such as silicon or germanium, is

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definitely more complicated. In fact, the needed process is not just a segregation, but a two-step process comprising a reducing reaction followed by phase separation. Phase separation of silicon and germanium has been reported starting from understoichiometric silicon oxide thin films obtained from physical vapour deposition, whereas no bulk material has been obtained at our knowledge by means of these or other methods. Indeed, as regards sol–gel strategies, strong oxygen understoichiometry is not easily achievable in glasses by sol–gel method, even by means of oxygen deficient precursors.

In this scenario, we have approached the task of producing Ge nanostructures in bulk silica by a sol–gel method, taking advantage of the high porosity and gas permeability of the material structure in the intermediate steps of the thermal densification process. As a matter of facts, we report for the first time the direct reduction of Ge nanostructures in silica by means of reaction of Ge-doped xerogels with reducing gases during sintering procedure.

2. Experimental details

Silica-based xerogel have been prepared with 2, 10, 20 mol% of germanium according to the following procedure: 6 ml of absolute ethyl alcohol are added under stirring with 2 ml of tetraethylorthosilicate, as well as the appropriate amount of germanium-tetraethoxide to reach the required Ge concentration in the matrix, and 1.2 ml of deionized water to start hydrolysis reactions. No catalyser is used since the presence of germanium precursor is enough to lead the sol gel transition in few days under thermostatic conditions at 40 °C in sealed plastic containers. After drying, samples are sintered with the following treatment: samples are heated from room temperature to 450 °C under oxygen atmosphere at a rate of 6 °C/h, then are kept at fixed temperature for 24 hours under Ar flux to replace oxygen with inert gas. Further heating to the final temperature (700, 800, or 900 °C) is then carried out either in Ar:CO or Ar:H₂ (2 vol% of reducing gas). Final samples are black coloured glassy disk 1 mm thick with a diameter of about 1.5 cm.

Powders of the samples have been analysed by X-ray diffractometry (XRD) to identify the chemical phases in the material, while micro-Raman spectroscopy on a fresh cut surface has been employed to investigate the spatial distribution of elemental germanium. Further measurements have been performed by means of transmission electron microscopy (TEM) on powdered samples in order to evaluate the size and morphology of crystalline domains of segregated germanium. XRD analysis has been carried out with a powder X-ray diffractometer Bruker D8 Advanced, working with Cu K α radiation, applying the Scherrer relation to estimate the mean size of the crystalline domains. Micro-Raman measurements have been performed with HeNe laser at 633 nm in backscattering configuration focused in a 1 μm sized spot, with a spectral resolution of 0.5 cm^{-1} and spatial sampling steps of about 50 µm, employing a Raman spectrometer Labram Dilor. High-resolution transmission microscopy images have been collected on powders by means of a FEI Tecnai G2 F20



Fig. 1. XRD patterns of Ge-doped sol-gel silica treated in CO (A) and in H_2 (B).

microscope, also performing diffraction and elemental analysis of the samples.

3. Results and discussion

XRD data in Fig. 1 show clear-cut differences between materials obtained from thermal treatment in Ar:CO and in Ar:H₂ atmosphere. Crystalline phases are detected in both kinds of samples, besides the broad peak from amorphous silica observed in sample treated in Ar:H₂, but reflections are different. Materials obtained after treatment in Ar:CO show reflections from crystallized SiO₂ in α -cristobalite phase, and only very weak peaks from elemental Ge (Fig. 1(A)). By contrast, thermal treatment in Ar:H₂ gives rise to samples where germanium in crystalline cubic structure is the unique segregated phase (Fig. 1(B)). The analysis of the peak width applying the Scherrer relation is consistent with crystalline domains with average size of about 20 nm, indicating the occurrence of nanostructuring throughout the material during the phase separation of elemental germanium.

Fig. 2(A) shows a representative high-resolution image of Ge nanostructures segregated in the amorphous silica matrix after H_2 reaction. Nanostructures so obtained really have crystalline domains of few tens nm, grouped in islands of slightly larger extension. Low resolution images, like that in Fig. 2(B), show that the size of Ge islands are of the same order of magnitude of silica porosity. Indeed, network porosity may have a key role in the nanoclustering size, because nanopores are in the same time an efficient interface for reaction with reducing gases, and also a suitable morphological unit for the nucleation of nanocrystals via trapping and deposition of volatile germanium produced by reaction. Formation of volatile products by reaction of dopant ions with reducing agents is indeed a typical cause of doping level decrease in silica-based materials.



Fig. 2. High-resolution (A) and low-resolution (B) TEM images of sol-gel Gedoped silica treated at 700 $^{\circ}$ C in Ar:H₂.

In this regard, mapping of microRaman phonon spectra along the sample thickness have been collected to get information on possible macroscopic inhomogenities or diffusion-limited spatial profiles of the coexisting phases. The Raman scattering spectrum is indeed a sensible probe of all the expected segregated phases, as shown in Fig. 3. The occurrence of cubic germanium in samples treated in Ar:CO (Fig. 3(A)) is confirmed by the narrow phonon mode at 300 cm^{-1} , well detectable despite the intense phonon spectrum due to α -cristobalite (peaks at 220 and 410 cm⁻¹). No trace of SiO₂ crystallization is instead observed in samples treated in Ar:H₂ (Fig. 3(B)). In this kind of samples, the Raman mode of cubic germanium falls at lower energy with a slightly larger peak width. Amorphous silica gives rise to a weak spectrum well detectable at the sample surface, mainly composed by broad structures with features at 440, 490, 606, 800, and about 1000 cm⁻¹, corresponding to silica Raman modes ω_1 , D_1 , D_2 , ω_3 , and ω_4 , respectively [12].

In Fig. 4, we report the variations of spectral features and intensity of the Ge Raman mode along the sampling profile across the sample thickness in material treated in Ar:H₂. Spectral position ν_{Ge} and full-width-at-half-maximum FWHM are nearly constant along the thickness, with ν_{Ge}



Fig. 3. Raman spectra of Ge-doped sol–gel silica after treatment in (A) Ar:CO and (B) Ar:H $_2$.



Fig. 4. Micro-Raman mapping of relative intensity (circles), FWHM (triangles), and spectral position (squares) of the cubic Ge Raman mode.

always below 300 cm⁻¹ and FWHM larger than 10 cm⁻¹. These facts indicates that segregated Ge is a nanometer sized phase throughout the sample, no matter what is the distance from the macroscopic free surfaces. In fact, Raman mode in bulk germanium is at 300 cm⁻¹ with less than 6 cm⁻¹ of FWHM, whereas ν_{Ge} values lower than 300 cm⁻¹ and FWHM larger than 6 cm⁻¹ are reported in the literature for Ge nanostructures [6,13,14]. Actually, Raman features like those in Fig. 4 were observed by other authors only at nanocrystal sizes smaller than 10 nm. However, those works clarify that compressive stress can partially compensate the Raman shift caused by phonon confinement [14], with consequent reduction also in the frequency broadening arising from size dispersion. Therefore, our Raman results together with XRD and TEM analyses point out a low contribution of compressive stress in

the Ge nanophase obtained by reducing treatment of sol-gel material.

Fig. 4 also shows that the relative intensity of the peak is nearly constant inside the material, but it decreases near the surfaces within a thickness of about 100–200 μ m. This result indicates that the reducing reaction efficiently involves the whole sample thickness with a common segregation mechanism likely driven by germanium volatility, as evidenced by Ge losses nearby the surface.

4. Conclusions

Reducing reaction of Ge-doped sol–gel silica with $Ar:H_2$ (and at a different extent also with Ar:CO) has been demonstrated to produce Ge nanophase embedded in a silica network. The particular features of the nanophase and the analysis of its spatial dependence mapped inside the bulk samples suggest that Ge nanoclustering may significantly be controlled during reaction by network porosity and Ge volatility.

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