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ScienceDirect

Solid State Communications 144 (2007) 429–432

solid state communications

www.elsevier.com/locate/ssc

Sol–gel synthesis of Ge nanophases in silica

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Received 25 July 2007; accepted 22 September 2007 by D.J. Lockwood

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.

PACS: 81.07.Bc; 81.20.Fw; 78.30.Hv; 61.46.Hk

Keywords: A. Nanostructures; B. Chemical synthesis; C. Scanning and transmission electron microscopy; E. Inelastic light scattering

1. Introduction

Semiconductor quantum dots (QD) 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 band-gap 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 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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0038-1098/$ - see front matter © 2007 Elsevier Ltd. All rights reserved.
doi:10.1016/j.ssc.2007.09.021

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:H_2 (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 Kα 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 microscope, also performing diffraction and elemental analysis of the samples.

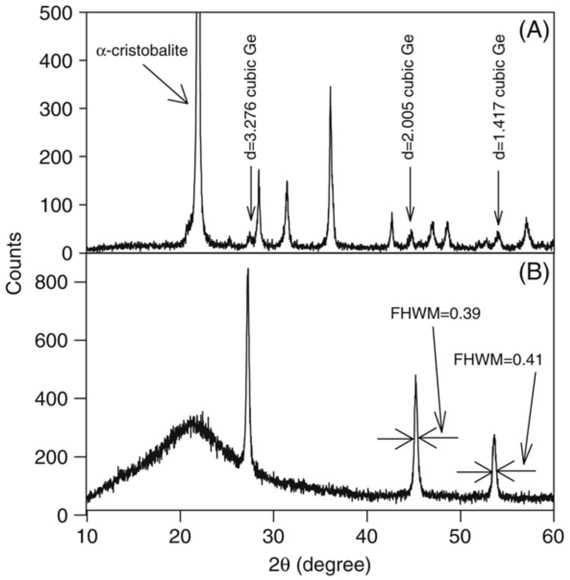

Fig. 1. XRD patterns of Ge-doped sol–gel silica treated in CO (A) and in H_2 (B).

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:H_2 atmosphere. Crystalline phases are detected in both kinds of samples, besides the broad peak from amorphous silica observed in sample treated in Ar:H_2, but reflections are different. Materials obtained after treatment in Ar:CO show reflections from crystallized SiO_2 in α-cristobalite phase, and only very weak peaks from elemental Ge (Fig. 1(A)). By contrast, thermal treatment in Ar:H_2 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.