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Near infrared absorption of Si nanoparticles embedded in silica films

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Abstract

The absorption coefficient of Si nanoparticles embedded in a silica matrix obtained through thermal annealing at 1000 °C of SiO thin films has been determined by a combination of ellipsometry and photothermal deflection spectroscopy. The high absorption level below 2 eV was explained by the superposition of the contribution of: (i) extended states and distorted bond states (Urbach tail), giving rise to an exponential regime of the variation of the absorption coefficient on energy and (ii) point defect states. The value of the characteristic energy of the exponential regime was found above 200 meV. This high value was partly related to the high stress present at the np-Si/SiO_2 interface. The point defects were attributed to dangling bonds and induced an additional absorption band located near 1.2 eV contributing to above 100 cm^{-1} to the absorption at this energy.

Keywords: Photon absorption spectroscopy; Silicon; Nanostructures; Interface states

1. Introduction

The emission properties of Si nanoparticles in silica have been extensively studied. The absorption properties below the fundamental gap have been much less studied, although background residual absorption may be an important parameter in applications relying on propagation of light in the near infrared (NIR) as in optical amplifiers [1] or lasers [2]. The main processes which contribute to absorption in amorphous Si (a-Si) below the band gap of Si are identified as distorted bonds giving rise to an exponential decrease of absorption with wavelength referred to as Urbach tail [3] and point defects giving rise to localized absorptions [4,5]. In the case of Si nanoparticles, the absorption coefficient below 2 eV has been determined by different optical methods. Photothermal deflection spectroscopy (PDS) was used in the case of very large particles obtained by laser induced crystallization of SiO_x ($x < 1$) [6]. An approach to the determination of the absorption has also been proposed through photoluminescence excitation (PLE) measurements [7,8]. As far as point defects are concerned, the signature of interfacial dangling bonds (P_b centers) has been observed by electron spin resonance (ESR) [7,9] or photoluminescence (PL) [10]. However, the influence of these absorption processes on the lineshape and the magnitude of the absorption coefficient α of Si nanoparticles in the visible-NIR has not been determined yet.

2. Experiment

$SiO_{x=1}$ films, 0.5 μm thick, were obtained by electron-gun evaporation of a commercial SiO powder in an ultra-high vacuum system. The films were deposited simultaneously on two types of substrates: (1 1 1) oriented Si wafer and fused silica substrate. The composition x of the films was measured by Rutherford backscattering spectroscopy (RBS) and found equal to 1. The films were annealed under vacuum at 800 °C for 2 h, then in nitrogen at 1000 °C for 1 h, revealing a phase separation between SiO_2 and Si-nc.

3. Results and discussion

Fig. 1 presents the Raman spectra of the layers after annealing at 800 °C for 2 h and one and two additional

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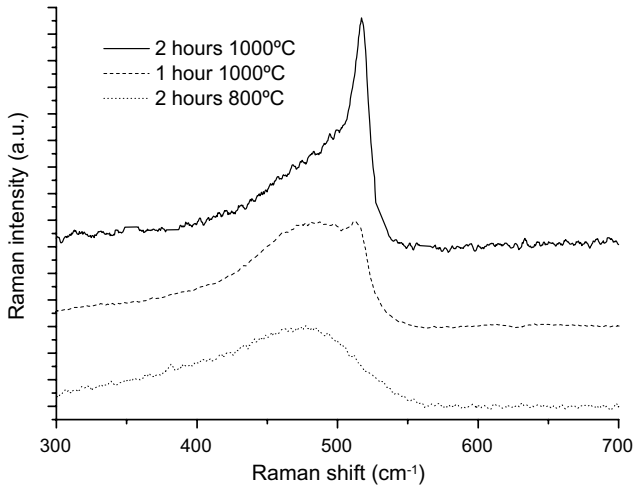

Fig. 1. Raman spectra for excitation at 488 nm of the sample after annealing at 800 °C for 2 h (dotted line), annealing at 1000 °C for 1 h (dashed line) and after two annealing steps of 1 h at 1000 °C (full line). A vertical offset has been applied to the spectra for clarity sake.

annealing steps of 1 h at 1000 °C. The Raman measurements were performed with excitation at 488 nm. In all cases a broad band centred near 480 cm^{-1} was observed. It corresponds to the signal of a-Si. At 800 °C, it means that the phase separation was in progress, with the appearance of amorphous np-Si. After annealing at 1000 °C, an additional peak near 520 cm^{-1} was observed, attributed to crystalline Si. The magnitude of the peak near 520 cm^{-1} increased with the annealing duration, showing that a larger amount of nanoparticles crystallised. However, a significant part of the signal attributed to a-Si remained present even after 2 h annealing at 1000 °C. Hence, the crystalline fraction extracted from Raman measurements amounted to only 15% after one step annealing at 1000 °C and reached a value of 42% after two steps annealing at 1000 °C. No evolution of the crystalline fraction was observed after additional annealing up to 10 h. The evolution of the films upon annealing has been confirmed by FTIR ellipsometry [11]. After annealing at 800 °C the peak in the imaginary part of the dielectric function, ε_2, corresponding to the position of the asymmetric stretching transverse optical mode (TO mode) of the Si–O–Si bridge, did not reach the position of SiO_2 showing the presence of a SiO_x matrix in which the Si-np were embedded. After annealing at 1000 °C for 1 h, the peak in ε_2 was close to the position observed in SiO_2 showing that the phase separation was effective with a SiO_2 matrix. However, with help of XPS measurements, the presence of a 0.4 nm thick SiO_x interface was evidenced, with $x = 1$. Same observations were made for two annealing steps at 1000 °C.

Transmission electron microscopy (TEM) was performed at an acceleration voltage of 200 kV on samples elaborated on the Si wafer. After annealing at 1000 °C, Si nanoparticles embedded in an amorphous matrix were observed. In some of them lattice fringes were imaged evidencing that a fraction of the nanoparticles was crystalline. The size distribution of the nanoparticles, as determined from the TEM micrographs, followed a lognormal distribution with an average size of 4 nm. The density of nanoparticles would be near 8×10^{18} nanoparticles cm^{-3}. It should be noted that in samples realised in similar conditions, other authors have evidenced, from energy filtered TEM, the presence of a large amount of amorphous nanoparticles [12].

Fig. 2 presents the photoluminescence spectra recorded at room temperature in the 1.2–2 eV range using the 488 nm radiation of an Ar laser as excitation. After annealing at 1000 °C a broad emission band centred at 1.3 eV was observed. Its position shifted to 1.38 eV upon one additional annealing. This position shift may be correlated with a better definition of the nanoparticle/matrix interface which would improve the confinement in the nanoparticles. These position values are in good agreement with the values found by others for nanoparticles of 4 nm [13]. However, the emission band position results from a combination of the size distribution of the nanoparticles and of size dependent luminescence efficiency, which increases with decreasing size. Hence the emission band position is a parameter which allows characterisation of our samples but which does not give necessarily the exact band gap value of nanoparticles of 4 nm in diameter.

Fig. 3 presents the electron spin resonance (ESR) spectrum recorded on the sample after two annealing steps at 1000 °C. A main absorption band was observed at $g = 2.0058$, which has been attributed to P_b centres at the np-Si–SiO_2 matrix interface in the literature [10]. We also observed a smaller contribution at $g = 2.0007$, also observed on a bare silica substrate, which is generally attributed to oxygen vacancies in silica and are referred to as E' centres. These last defects may also be present in the SiO_2 matrix around the Si-np but should not contribute to the absorption measured.

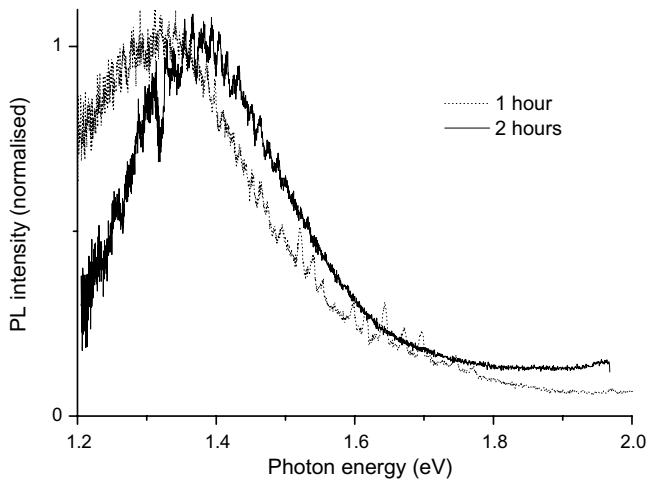

Fig. 2. Photoluminescence band recorded with excitation at 488 nm. A broad band was observed, centred near 1.3 eV after one annealing step and 1.38 eV after two annealing steps at 1000 °C.