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Optical properties of Si nanocrystals self-nucleated onto SiO_2 surfaces

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SiO_2/Si heterolayers were synthesized employing a RF magnetron sputtering system. For thin Si layers, it is shown that intrinsic voids on the SiO_2 surface act as nucleation sites, promoting the formation of nanocrystals (NCs). As the deposition time of the Si layer increases it is observed that the influence of the SiO_2 texture on the nucleation of Si nanocrystals diminishes. Studies carried out on samples grew on glass substrates shown that control in the NCs sizes allows to control the absorption edges of the synthesized samples between 300 and 700 nm. As-growth samples shown two photoluminescence bands around 570 and 660 nm, a band in the infrared region shows up and shifts toward the visible region as the Si layer thickness decreases.

Keyword: Nanoparticles; Silicon ligth emission; Optoelectronics

1. Introduction

Si nanocrystals (Si NCs) have received considerable attention because its potential applications in optoelectronic and display devices [1,2]. It has been suggested the use of Si NCs into spin-on-glass SiO_2 to serve as a down-converter of high energy photons [3,4]; photons in the blue region could be absorbed by Si NCs and emitted via photoluminescence mechanisms in the red region and then the spectral response would be improved.

Si NCs has been synthesized using almost all the techniques available to the materials science. The growth of Si-rich SiO_x (x<2) films is one of the most popular approaches because it is inherently a free contaminant deposition method. The formation of films is generally followed by thermal annealing processes focusing in to suppress defects to generate Si aggregates and to crystallize them.

Previous results have showed that the growth of thin CdTe films on SiO_2 promotes the appearance of CdTe crystalline facets influenced by the SiO_2 texture [5]. In this paper, we generalize the approach depositing SiO_2/Si heterolayers employing a radio frequency magnetron sputtering system. We grew several samples varying de deposition time of the Si layer. The results showed clearly that voids in the SiO_2 are nucleating sites for Si NCs. The absorption edge of the samples is varied from 600 to 350 nm by adjust the Si time deposition. All as-grown samples showed two photoluminescence (PL) bands around 570 and 670 nm, while a third band in the infrared region shows up and shift toward the visible region as the Si time deposition reduces. The absorption and PL properties were related to the presence of Si NCs. The characterization of the samples allows us to establish that the influence of the SiO_2 texture as a nucleation promoter is lost as the thickness of the Si layer increase.

2. Experimental Details

A set of SiO_2/Si heterolayers was synthesized employing a radio frequency magnetron sputtering system. The samples were grown from a polycrystalline Si target and deposited on Si (100) and low-cost glass substrates heated at 400 °C. The SiO_2 films were grown by reactive sputtering of the Si target employing a plasma mixture of 25% oxygen (O_2) and 75% argon (Ar); the Si layer was deposited whereas the oxygen flow was shutting off. The total gas pressure in the chamber was kept constant at 15 mTorr during the deposition process. The RF power applied to the target was 100 W. After the deposition of each layer, the plasma was turned off and the chamber was evacuated to 10^{-7} Torr. We prepared five samples adjusting the time of deposition of the Si layers at 600 s, 450 s, 300 s, 150 s and 60 seconds. When the growth was finished, the samples were maintained inside the system until room temperature was attained.

The structure of the samples was evaluated by transmission electron microscopy (TEM) employing a TITAN system, equipped with a field emission electron gun operated at 300 kV. The crystallographic properties of the samples were studied by X-ray diffraction carried out in a Siemens D5000 system employing the Cu K_α wavelength; with a grazing incidence angle of 3°. The infrared (IR) spectra were obtained with a Nicolet 750 FTIR system. Micro-Raman spectroscopy was carried out in a Horiba Jobin Yvon LabRAM system employing the 488 nm line of an Ar+ ion laser as excitation source. Optical transmission measurements were obtained using a Perkin Elmer Lambda 40 UV-Vis spectrophotometer. Room temperature PL spectroscopy was carried out employing a standard setup controlled by a personal computer and a 473.8 nm laser diode as excitation source.

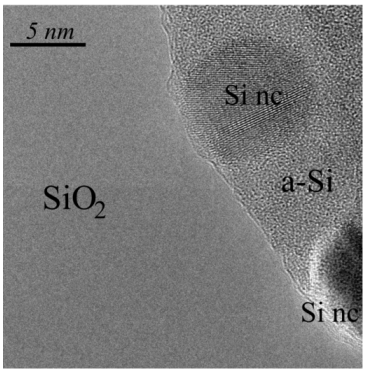

Figure 1. TEM image of the 600s sample.

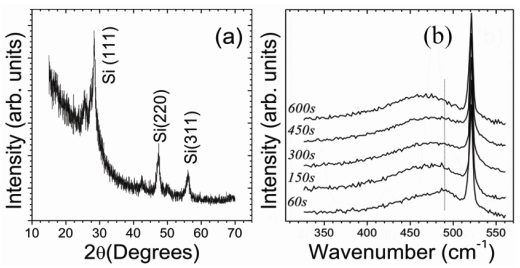

Figure 2. (a) Representative X-ray diffractogram (XRD) of sample 600s and (b) Raman spectrum of the SiO_2/Si samples.

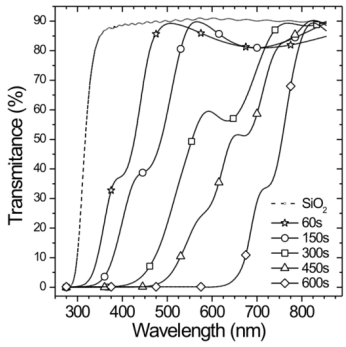

Figure 3. UV-Vis transmittance spectra of the SiO_2/Si samples. The absorption spectra of a SiO_2 film is also included as reference.

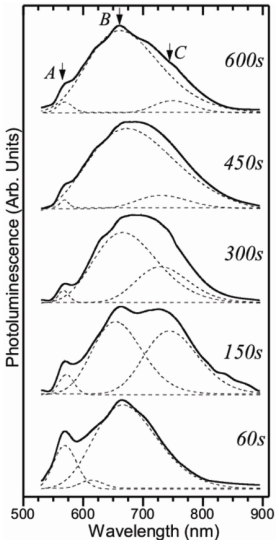

Figure 4. Room temperature photoluminescence spectra of the SiO_2/Si samples.

3. Results and Discussion

TEM bright field of the 600s sample is presented in fig 1. The micrograph shows the presence of a well defined Si layer on a SiO_2 film. TEM analysis showed that the Si layer is predominantly amorphous, but it contains a large number of Si NCs nucleated on the SiO_2/Si interface.

It is know that the region near to surface voids or corners generate stress gradients and are locations of instability for the thin films deposit [6]. The effect of mechanical stress on solid phase crystallization is still a matter of debate, but it is believe that a small amount of compressive stress favors the crystallization due to the volume contraction typically observed [6]. In our approach, compressive stress is likely present; first because sputtering deposits intrinsically compressive films [7] and second, because the coefficient of thermal expansion is nearly an order of magnitude larger in Si than in SiO_2 [7], leading compressive stress in the Si layer during the growth (carried out to 400°C) when cluster formation is most likely to occur. These conditions favor the coalescence of atoms into Si NCs and can explain why it is observed in voids zones of the SiO_2.

Figure 2a shows the X-ray diffractogram (XRD) of the sample 600 s, this XRD is representative of the whole set. The peaks were indexed using the powder diffraction file 271 402 for cubic silicon. The peaks corresponding to the (111), (220), and (311) planes could indicate the presence of clusters of silicon. The fact that all XRD show a same intensity in the peaks corroborates that the cluster nucleation is promoted only on the SiO_2 surface [8].

Figure 2b shows the Raman spectra of the SiO_2/Si heterolayers. The peak at 521 cm^{-1} corresponds to the crystalline Si. The broad band around 480 cm^{-1} in the Raman spectra can be related to amorphous characteristics in the silicon interlayers [9]. This band becomes broader and shifts toward lower wavenumbers as the Si layer thickness increase; indicating a higher structural disorder [9]. The characteristics of the Raman spectra could be considered contradictory as compared with the features observed in the X-ray diffractograms however those are due to the presence of nanocrystals. The above mentioned results indicate that the influence of the SiO_2 texture on the nucleation of Si NCs is diminishing as the thickness increases.

The IR spectrum of the samples, not presented here, showed the characteristic bands related to the rocking, symmetric stretching and asymmetric stretching vibration modes of the oxygen atom in the Si–O–Si group. The features of the IR spectra indicated that the composition of the oxide matrix corresponds to that of SiO_2 [10]; discarding the presence of absorbing or luminescent centers related Si-O covalent bonds in the interface Si NCs/SiO_2.

A fundamental contribution of this work is the synthesis of Si NCs embedded in SiO_2 showing a well controlled optical absorption through the entire visible spectral range. Figure 3 presents the UV-Vis spectra of the samples grown on glass substrates. A first aspect to be noted is that all

samples show well defined absorption edges, without the presence of absorption bands related to O bonds in the SiO_2/Si NCs interface [11]. This show that the NCs embedded in the samples has a low level of oxidation on its surface [11]. The sample 60s shows the absorption edge at highest energy. In accord with the effective mass theory of quantum confinement, as the Si NCs becomes larger the absorption edge shifts systematically toward lower energies. However, it must be noted that even the 600s sample shows an absorption edge at higher energy than of bulk Si.

All the samples showed room temperature PL emission without any thermal treatment; the spectra are presented in figure 4. The PL can be related to radiative recombination in Si NCs of different size [12]. A detailed analysis showed that all spectra are comprised of three Gaussian bands (dotted lines) with different relative intensities, named peaks *A*, *B*, and *C* respectively [12]. It was found that the *A* and *B* contributions remain located at 570 and 660 nm respectively for all PL spectra. In contrast, the Gaussian *C* is shifted toward lower wavelength as the Si thickness increase.

4. Conclusions

The growth of SiO_2/Si heterolayers by RF reactive sputtering is a direct method to obtain room temperature photoluminescence emission from as-grown Si NCs. We found that the influence of the SiO_2 texture as a nucleation promoter decreases as the thickness of the silicon interlayer increases. The absorption edge of the samples is shifted toward lower energies as result of the gradual growth of bigger Si NCs far from the SiO_2/Si interface.

The control of NCs size and its influence on the absorption edge of the SiO_2/Si/SiO_2 layer could be employed as a down conversion layer useful in photovoltaics systems.

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