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Review

Optical study of annealed cobalt–porous silicon nanocomposites

M.-B. Bouzourâa [a], M. Rahmani [a,*], M.-A. Zaïbi [a,b], N. Lorrain [c], L. Hajji [c], M. Oueslati [a]

[a] Unité de Nanomatériaux et Photonique, Faculté des Sciences de Tunis, Département de Physique, 2092 El Manar, Tunis, Tunisia
[b] Ecole Supérieure des Sciences et Techniques de Tunis, 5 Avenue Taha Hussein, 1008 Tunis, Tunisia
[c] Université Européenne de Bretagne, CNRS FOTON-UMR 6082, 6 rue de Kérampont, BP 80518, 22305 Lannion, Cedex, France

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ABSTRACT

We report Raman and photoluminescence studies of cobalt–porous silicon nanocomposites (PS/Co). Cobalt was introduced in porous silicon (PS) by immersion method using $CoCl_2$ aqueous solution. The presence of cobalt in PS matrix was identified by FTIR spectroscopy and EDX analyses. The Raman spectroscopy revealed the presence of Si bonded to cobalt oxide in PS/Co. We discuss also the Raman spectra of PS and PS/Co samples under different annealing temperatures ranging from room temperature (RT) to 600 °C. The optical properties of PS and PS/Co were studied by photoluminescence (PL). The highest PL intensity was observed for an immersion time of 60 min. For long duration, the deposited cobalt quantity acts as energy trap and promotes the non-radiative energy transfer; it is the autoextinction phenomenon. We have studied also the effect of the annealing temperature on the PL of both PS and PS/Co samples. For PS, the annealing process leads to a rapid oxidation of the Si nanocrystallites (nc-Si). In the case of PS/Co sample, two different mechanisms are proposed; one is the desorption of Si–$H_{x(x=2,3)}$ with the formation of cobalt oxide for annealing temperature less than 450 °C which causes the increasing of PL intensity and the stability of PL energy, the other mechanism is the transformation of the porous silicon to silica at high temperatures (>450 °C) which leads to the decreasing of the PL intensity and the blue shift of the PL curve.

Contents

1. Introduction

The highly efficient luminescence of porous silicon at room temperature [1] makes it an interesting material for various applications in optoelectronic devices like light emitting diodes (LED).

The doping of porous silicon with some kind of metals is essential for the creation of nanocomposites with multifunctional properties. Indeed, transition-metal ions such as Fe^{3+} or Co^{2+} introduced in porous silicon (PS) layer may provide new nanomaterials with optical, electrical and magnetic properties. Doping methods such as immersion or electrodeposition are currently used and must be followed by a thermal treatment in order to promote the insertion of the transition-metal ions inside the porous matrix and to form metal oxides at the porous surface.

Some investigations [2–4] have focused on the PL variation of porous silicon as a function of annealing temperature. Among these studies Roy et al. [2], reported that the PL peak position and the PL intensity have non-monotonic variations with increasing temperature. They indicated also that the origin of the PL can be explained by a model which incorporates both nanostructures åfor quantum confinement and silicon complexes with defects

* Corresponding author. Tel.: +216 278 10093; fax: +216 718 85073.
E-mail address: rahmanimehdi79@yahoo.com (M. Rahmani).

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interfaces as luminescent centers. In another work, Wiemer et al. [3] have investigated the effects of annealing temperature and surface preparation on the formation of cobalt silicide interconnects. The authors reported that Raman peaks detected between 200 and 230 cm^{-1} were corresponding to a CoSi layer formed using a rapid thermal process. In, another work which focused on the cobalt silicide films [4], the elaborated films were analyzed by Raman spectroscopy which showed an intense peak at 670 cm^{-1} attributed to cobalt oxide formed by oxygen from air and the unreacted cobalt on the sample surface. From these different works, we noted that the cobalt–silicon layer has interesting physical properties such as a high thermal stability and a low bulk resistivity and then it can be employed for several applications in microelectronics and optoelectronics.

In this paper, we have introduced cobalt ions in the PS matrix and we have focused our interest on the effect of the annealing temperature on the optical properties of cobalt–porous silicon å (PS/Co) nanocomposites using photoluminescence (PL) spectroscopy. Furthermore, we have followed the surface modifications of PS and PS/Co samples with temperature variation using FTIR spectroscopy. These modifications have been confirmed, also, by Raman spectroscopy. Complementary studies using Energy dispersive åX-ray analysis were carried out to estimate the cobalt concentration through the depth of the porous layer.

2. Experimental

Samples were elaborated from a boron-doped p-type Si(1 0 0) substrates with 0.1–2 Ω/cm resistivity. First, an ohmic contact has been formed by coating the backside of the silicon wafer with aluminum (Al) and subsequently annealed at 500 °C for 30 min. The porous silicon was prepared using electrochemical anodisation in HF solution (40%)/C_2H_5OH/H_2O (2:1:1), the current density was 10 mA/cm^2 and the etching duration was fixed at10 min. The freshly PS layer was then immersed in an aqueous solution of cobalt chloride with a low concentration fixed at 0.5 M during an optimal duration of 120 min, maintained at RT. To eliminate the residual molecules and gases, the samples have been dried by nitrogen gas. For a thermal treatment in air, the sample was introduced in a programmable furnace maintained at the desired annealing temperature during 5 min. Then, it was taken out of the furnace and cooled to RT in order to record both Raman and PL spectra at the same spot of the sample. The Raman and PL spectra were recorded using a micro-Raman spectrometer (Jobin-Yvon confocal micro-Raman T64000) with a resolution of 0.1 cm^{-1} and the recording time was set equal to 60 s. The pumping source for PL and Raman measurements was the 488 nm argon laser line fixed at a power of 50 mW. The FTIR analyses are taken on transmittance mode and investigated in the 400–4000 cm^{-1} range with a 2 cm^{-1} step using Bruker IFS66v/s FTIR spectrometer. In order to estimate the Co atomic percentage (at%) in the porous layer, scanning electronic microscopy (SEM) observations and energy dispersive X-ray (EDX) analysis were performed on the cross-section of the sample at different depths using a JEOL JSM-5600 LV. The estimated error for each concentration variation was at most 0.3% taking into account the doping inhomogeneity of the sample. The scanned surface is about 1 μm^2 with a resolution of 1 μm.

3. Results and discussion

The FTIR spectroscopy was performed at RT on PS/Co before and after annealing process and compared to that obtained on PS (Fig. 1). For PS, the principal recorded vibration bands are located

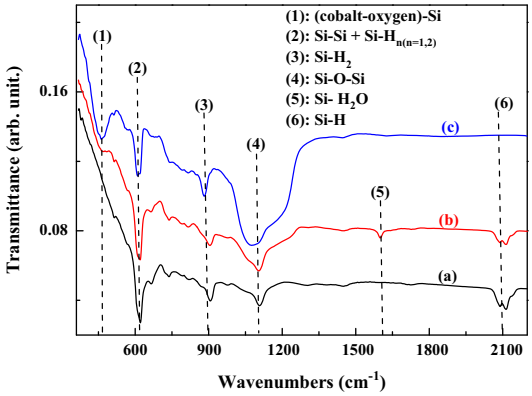

Fig. 1. FTIR spectra of PS (a), PS/Co before annealing (b) and PS/Co after annealing at 400 °C (c).

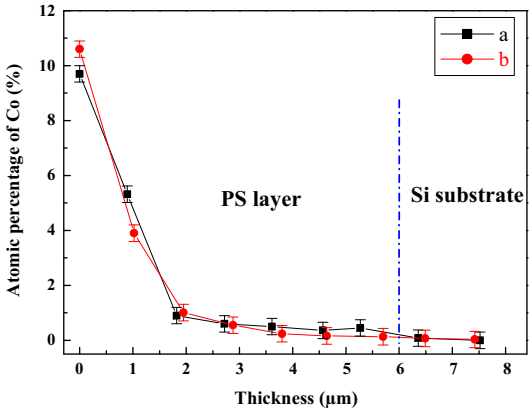

Fig. 2. Atomic percentage of cobalt at different depths of the PS/Co layer from the top surface to the Si substrate deduced from EDX measurements before annealing (a) and after annealing at 400 °C (b).

at 620 cm^{-1} which is related to a mixture of stretching wagging mode Si–Si and wagging mode Si–$H_{n(n=1 \text{ and } 2)}$,900 cm^{-1} attributed to scissors mode Si–H_2. A large vibration absorption band is observed at 1100 cm^{-1} corresponding to stretching mode Si–O–Si. Moreover, the spectrum also shows the presence of a vibration band at 2120 cm^{-1} indicating the presence of Si–H bond in which the Si atom is back bonded to another Si atom [5,6]. A new vibration band at 470 cm^{-1} was appeared after PS immersion in $CoCl_2$ aqueous solution. Generally, (metal–oxygen)–silicon bonding is expected between 300 and 700 cm^{-1} [5,7–9], therefore the band at 470 cm^{-1} can be attributed to (cobalt–oxygen)–silicon bonding. We also observe a band at 1600 cm^{-1} corresponding to molecular water vibration [7], these species coming from the aqueous solution. After annealing process, the intensity of the band at 470 cm^{-1} has increased indicating the formation of a large quantity of cobalt oxide. We also observe, for higher annealing temperatures ($T = 400$ °C), the disappearance of the band corresponding to molecular water and the increase of the Si–O–Si vibration band. On the other hand, the annealing process does not affect the Si–Si and Si–H_2 vibrations. This result indicates that Si–H_2 bonds remained at temperature more than that found in the case of the adsorption on Si(1 0 0) surface [10].

To confirm the FTIR results, SEM observations and EDX analysis were performed on the cross-section of PS. The results show that the porous layer thickness was about 6 μm. The EDX analysis, performed at different depth of PS/Co layer before and after annealing at 400 °C, reveals that the atomic percentage of cobalt decreased from the top to the bottom of the layer (Fig. 2). The large amount of Co is deposed at the surface. The Cobalt concentration