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Review

Enhancement of porous silicon photoluminescence by electroless deposition of nickel

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ABSTRACT

Nickel-porous silicon nanocomposites (PS/Ni) are elaborated by an electroless deposition method using $NiCl_2$ aqueous solution. The presence of nickel ions in the porous layer is confirmed by Fourier Transformed InfraRed spectroscopy (FTIR) and Raman spectroscopy. The photoluminescence (PL) spectra of PS/Ni, prepared at different electroless durations (t_{edp}), are analyzed. A remarkable enhancement in the integrated PL intensity of PS containing nickel was observed. The lower t_{edp} favor the deposition of nickel in PS, hence the silicon dangling bonds at the porous surface are quenched and this was increased the PL intensity. However, for the longer t_{edp}, the PL intensity has been considerably decreased due to the destruction of some Si nanocrystallites. The PL spectra of PS/Ni, for t_{edp} less than 8 min, show a multiband profile indicating the creation of new luminescent centers by Ni elements which induces a strong modification in the emission mechanisms.

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1. Introduction

After the observation of highly efficient visible photoluminescence (PL) at room temperature from porous silicon (PS) by Canham [1], this material has become an attractive material in electronics and optoelectronics fields. The structure of the PS consists of a network of silicon nancrystallites (nc-Si) that depends on several external factors such as air and storage conditions. In fact, the freshly prepared PS is passivated by hydrogen and its exposure to ambient air causes the progressive modification of the hydrogenated surface by oxidizing the nc-Si. The oxidation may modify the structure of the nc-Si surface and then its optical properties are affected [2,3]. To overcome the structural problem and to improve the PL of PS in order to introduce it in practice devices, it is necessary to change the composition of the PS surface by incorporating some elements. Transition metals like iron, cobalt or nickel and necessarily others can be easily introduced inside the silicon pores [4–7]. Many researchers have investigated the optical properties of porous silicon doped with iron [4,5,8]. Among these studies, Miu et al. [9] have analyzed the PS impregnated in iron ion solution and they proved, by SEM and EDAX measurements, that the iron elements are distributed inside the pores network and they are located in the nc-Si. Also, Rahmani et al. [4] reported that Fe ions are deeply incorporated in PS matrix by an impregnation method. The authors demonstrated also that PL intensity of PS is enhanced due to the passivation of the silicon nanocrystallites by iron which induces two energy levels localized in the PS band gap. Other studies

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[10–12] are interested to the structural properties of PS-iron nanocomposites. Recently, Bouzourâa et al. [6] have deposited cobalt on the PS surface using immersion method, they found that cobalt ions generate a radiative recombination centers which enhance the PL intensity more than three times compared to that of PS. From these works, we noted that the transition metals contributed to the emission mechanisms in PS and they present an important role in the stabilization of the porous structure. On the other hand, the interest in nickel oxide thin films has been fast growing due to its importance in many applications in science and technology. The oxide nickel film (NiO) exhibited p-type semiconducting nature, with wide stable band gap in the range of about 3.71 eV [13] which allowing it to be used as a transition metal oxide. The NiO can be employed in many fields [14–17] as an active electrode in electrochromic devices, magnetic materials, solar cells and functional sensing layer for developing chemical sensors. There have been many reports discussing the magnetic and electrical properties from Ni-PS or NiO-PS nanostructure [7,18,19]. However, there are a few investigations on the optical properties of NiO [13,20].

We also note that several porous structures were studied such as porous alumina doped with rare earths [21], these nanocomposites have an intense green PL related to Tb^{3+} ions. In other work [22], the authors investigated the optical properties of SiGe nanocrystals prepared by electrochemical anodization of SiGe Layer grown by ultrahigh vacuum chemical vapor deposition. Therefore, the porous materials have a fundamental and a technological importance and they possess interesting optical properties due to quantum confinement effects.

In this work, we have focused on the studying of nickel/porous silicon nanocomposites elaborated by the electroless deposition method in order to obtain an enhancement of the PS photoluminescence. Characterization is carried out by Fourier Transformed InfraRed (FTIR) spectroscopy, Raman and photoluminescence (PL) spectroscopy.

2. Experimental

Before the elaboration of porous silicon, an ohmic contact was formed by coating the backside of the silicon wafer with aluminum (Al) and subsequently annealed at 500 °C for 30 min. The used wafer was a boron-doped p-type with (100) orientation and 0.1–2 Ω cm resistivity. The porous layer was formed by electrochemical anodisation on the polished surface of the wafer. The elaboration was performed in dark with an etching current density of 10 mA cm^{-2} using an electrolyte of HF(40%)/C_2H_5OH/H_2O (2:1:1) during 8 min. These elaborated conditions allow obtaining a PS of 60–70% porosity [23] and a thickness layer of about 6 μm [4]. The introduction of Ni ions into the porous layer was performed by the electroless method using a $NiCl_2$ aqueous solution. The concentration of nickel chloride was fixed at 0.1 M and the current density applied was 0.6 mA cm^{-2} after reversing the generator terminals. The electroless duration was varied from 0 to 11 min. The elaborated samples have been dried by nitrogen gas in order to eliminate the residual molecules and gases. The FTIR analyses are taken on transmittance mode using Bruker IFS66v/s FTIR spectrometer and investigated in the 400–4000 cm^{-1} range with a step of 2 cm^{-1}. The 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 measurements was the 488 nm argon laser line fixed at a power of 50 mW. All the measurements were carried out at room temperature. The laser line having a wavelength of 488 nm is suitable to excite the majority of sizes nc-Si, for this reason it is usually used to perform PL measurements of PS.

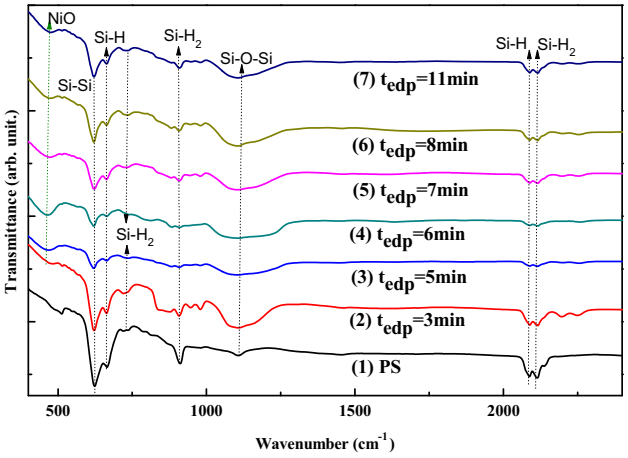

Fig. 1. FTIR spectra of PS and PS/Ni samples with different electroless durations.

3. Results and discussion

The FTIR analysis were performed on PS/Ni at different electroless durations t_{edp}, the spectra are shown in Fig. 1. The principal recorded vibration bands, observed in both spectra, are 910 cm^{-1} corresponding to Si–H_2 scissors mode, 1106 cm^{-1} attributed to Si–O–Si stretching mode, a large vibration absorption band at 620 cm^{-1} which is a stretching wagging mode Si–Si, a stretching mode of Si–H at 664 cm^{-1} and a wagging mode of Si–H_2at 737 cm^{-1} [3]. We also showed three peaks at 2088 cm^{-1}, 2111 cm^{-1} and 2138 cm^{-1} attributed to Si–H, Si–H_2 and Si–H_3 stretching modes, respectively [3,24]. For the PS sample, the weak peak at 510 cm^{-1} has been recorded but it could not be identified from the infrared data available in literature. Noting that Zhao et al. [25] have been well recorded the same peak by examining the influence of the microstructure on the optical properties of PS. After Ni deposition on PS at different t_{edp}, the FTIR spectra is, practically, the same that of PS. The intensity of many bands are diminished especially that of Si–Si and Si–$H_{n\ (n=1-3)}$, while the band of Si–O–Si stretching mode became larger than that of PS. The band at 510 cm^{-1} has been disappeared to the detriment of a new band at 468 cm^{-1}. Many works [26–29] showed that metal-oxygen–silicon banding is expected between 300 cm^{-1} and 700 cm^{-1}. Then, the new band at 468 cm^{-1} is certainly assigned to (nickel–oxygen) – silicon banding. The increase of t_{edp} up to 6 min induced the growth of Ni–O band intensity and beyond this time it decreased. This result demonstrates the reduction of Ni–O species on nc-Si for high electroless durations.

The Raman spectra of PS and PS/Ni samples, elaborated at different electroless durations are presented in Fig. 2a. Raman spectroscopy is a non-destructive technique which provides information on the vibrational properties of metal-oxide-semiconductor materials. In the present work, this spectroscopy has been used to characterize the chemical composition of PS and PS/Ni surfaces. The corresponding spectrum to PS (Fig. 2a) is characterized by many peaks situated at 150 cm^{-1}, 300 cm^{-1}, 509 cm^{-1}, 521 cm^{-1} and a large band centered at 950 cm^{-1}. The large band recorded at 920–980 cm^{-1} is ascribed to the presence of Si–OH and SiO_3 stretching mode [6]. The two peaks, at 150 cm^{-1} and at 300 cm^{-1}, correspond to one and two phonons TA vibration mode of the silicon network, respectively [6]. Recalled that these peaks are recorded only if the wevectors of phonons (q) are extended from 0 to $(\hbar)/(L)$ where L is the nc-Si size.

The interesting result of PS Raman spectrum is to have the main peak composed on two separated vibration modes (Fig. 2b), this result indicates that the analysis is doing near the PS/Si interface [24]: (i) the first one is a net peak at 521 cm^{-1} arises from LO and TO phonon modes which are degenerated at the Brillouin zone center (Γ-point: phonon wavevector ≈ 0) [30]. (ii) The second one is an