Enhancement of porous silicon photoluminescence using (Ni) treatment

M Nabil1,*, M Elnouby1, N Gayeh2, A H Sakr2 and H A Motaweh2

1Advanced Technology and New Materials Research Institute, City for Scientific Research and Technology Applications, New Borg El-Arab City, Alexandria, 21934, Egypt.
2Department of Physics, Faculty of Science, Damanhour University, Egypt.

Abstract. A new method has been developed to improve the photoluminescence intensity of porous silicon (PS). Self-organized (PS) can be used in various fields. The deposition of metal nanoparticles (Ni) allows utilizing the obtained nano-composite for numerous applications such as sensor technology, biomedicine, and many more. (Ni/PS) nano-composite powders are prepared using Ni deposition on the PS powder surface. The (Ni/PS) powders became hydrophilic by the deposited Ni nanoparticles. At the different percentages of (Ni:PS), at a higher percentage than (3:1) the values of the crystallite size of Ni and PS are nearly equivalent which suggests the saturation case of PS surface by Ni particles. It also depends on the deposition time value. In this study, that is the commercialization of nanostructured materials, it is important that the manufacturing costs are appropriate and inexpensive for large scale production, in addition, the enhancement of the photoluminescence intensity of (PS).

1. Introduction

Crystalline Silicon (c-Si) (as an indirect semiconductor), which is a non-emitted light. And so it is many alternative materials have been proposed to improve the luminescence from silicon-based materials [1]. Porous silicon (PS) is a versatile material whose fundamental properties is of value to diverse fields, a consequence of specific properties such as visible light emission, tunable surface chemistry, huge surface area, and controllable morphology. Due to its variable pore-size, PS is a suitable host material for loading other nanosized structures, e.g., small molecules, metals, and magnetic nanoparticles, thereby adding properties of the confined spaces to the pores [2]. PS can be considered as a silicon crystal having a network of voids in it. The nanosized voids in the silicon bulk result in a sponge-like structure of pores and channels surrounded by a skeleton of the crystalline Si nanostructure [3]. For improving the electroluminescence and the photoluminescence intensity of PS, several passivation methods have been proposed. [1]

It has been demonstrated that PS with high surface areas may be easily prepared by a simple, safe Chemical technique, which is more energy efficient, cost-effective, and time-saving. Various techniques have been considered to prepare nanocomposite materials, including thermal, plasma spraying and physical and chemical vapor deposition. Among these methods that is widely used, chemical deposition, which offers several advantages when compared with other techniques including precise control, low energy requirements, uniform deposition, low cost in production of large area samples, good reproducibility, versatility, capability to coat complex component geometries, high production rate and reduction of waste. [4]

In one such attempt, attention was focused on nanoparticles-silicon composite materials. Many materials such as silver, gold and the transparent conducting oxides such an indium tin oxide, were
tested and proved their ability to improve the PS properties. Also, various metals are deposited onto the PS surface using several techniques as the immersion plating technique or dipping the surface into a solution containing metal ions such as Ag, Cu and Pd [1]. Noticeable, only a few reports are describing the incorporation process of Nickel (Ni) nanoparticles and the surface of a silicon wafer, followed by manipulation of surface chemical bonds. The most useful technique is the deposition from the liquid phase by chemical method, which is actually used in this research as a result of the precipitation process of metal particles "inside and surroundings" of pores. The solution can penetrate the whole porous structure providing the deposition along the full length of the pores. However the deposition process may be complicated by capillary effects and non-uniformity of porous structure.

In the present work, for the first time the (Ni /PS) nanocomposite is prepared in powder form, which facilitate of using in many applications in several fields. In addition, the possibility to enhance PS photoluminescence intensity using chemical techniques for producing the nanocomposite material of PS and (Ni). The properties of the prepared nanocomposite material were studied by various characterization methods such as Raman spectroscopy, FTIR, XRD and Photoluminescence spectra.

2. Material and methods
Firstly: Beginning with commercial Si powder, PS powder was prepared using a stain-etching method, depending on our previous study [5], using alkaline medium. Then, the PS powder was filtered out from the etching solution and dried at 40 °C overnight. With this procedure, the porous layer was formed on the Si powder surface. Secondary: nano-Ni layers were deposited on the PS powder by a chemical deposition technique. The prepared PS powder was immersed in an aqueous NiCl₂ solution at 80 °C for several (Ni salts: nPS) concentration percentages. Then, nano-Ni was deposited on the PS surface via redox reactions, i.e., Ni ions in the solution were reduced and PS layers were simultaneously oxidized. Finally, the nanocomposite (Ni/PS) powder was filtered out again from the Ni salt solution and dried at 60 °C overnight for two days.

The structure and morphology were characterized using XRD (X-ray 7000 Schimadzu diffractometer). The formation of PS chemical bonds was determined using FTIR (Fourier Transform Infrared Spectrophotometer- Shimadzu FTIR -8400 s, Japan), Raman Spectroscopy (Senteral - Bruker Raman micro-spectroscopy), UV-Vis. Spectrophotometer Double Auto cell (Labomend. INC, USA) and PL (Cary Eclipse Fluorescence Spectrophotometer Photoluminescence- American) analysis of PS, before and after treatment with (Ni).

3. Results & discussion
Figure 1 shows the XRD peaks in the range 20 = 20°–100° for the (Ni/PS) samples at different Ni salt concentrations. As can be seen, the (Ni/PS) samples shows the diffraction peaks of (PS) at 2 (= 28.23°, 47.193° and 56.23° corresponding to Si (111), Si (220) and Si (211), respectively. In addition, some weak diffraction peaks at 2θ = 76.68°, 88.34° and 95.24°, corresponding to the Ni (220), (201) and Ni (311) planes, respectively \{JCPDS card 27−1402 and 45-1027, corresponding to Si and Ni, respectively\}. Figure 1.a shows the appearance of Ni planes, that in case of the double percentage of the Ni salt concentration with respect to the presence of a PS weight percentage (2 Ni: 1 PS). Noticeable, the decreasing of the Si peak intensities, as a result of the increasing Ni salt concentration at the same value of PS weight percentage (3 Ni: 1 PS), as shown in figure 1.b. Figure 1.c shows the re-increasing in the XRD peak intensities of Si and Ni, which indicates the increasing of Ni layer thickness on the PS surface as increasing of Ni salt concentration till PS surface saturation. In addition, figure 1 shows the directly proportional between the Ni layer and the deposition time (t).
Figure 1. XRD patterns of (Ni/ PS) nano-composite powder chemical deposition process, at (a) {(2Ni: 1 PS) at 30 min}, (b) {(3Ni: 1 PS) at 120 min} and (c) {(4Ni: 1 PS) at 120 min}.

Table 1 shows a comparison between the diffraction peaks of Si and Ni. The intensity of XRD signals, which is used for the calculation of the average size of the PS, using Scherrer's equation [3]. It is well known that the crystallite size can be estimated from diffraction pattern analysis by measuring the full width at half maximum (FWHM) measurement and applying the Scherrer’s equation:

\[ d = \frac{k \lambda}{B \cos \theta} \]  

Where B is the FWHM, K is the Scherrer constant (1 > K > 0.89), λ is the wavelength in nanometers, and d the mean crystallite size.

Table 1, also, displays important notes about the smallest value of the crystallite size, which is corresponding to the percentage (3 Ni: 1 PS). In addition, at (4 Ni: 1 PS) percentage, the values of the crystallite size of Ni and PS are nearly equivalent.

Table 1. Typical XRD diffraction peaks of (Ni/ PS) nano-composite powder obtained by electro-less technique.

| (Ni: PS) | Crystallite size of PS (nm) | Crystallite size of Ni (nm) |
|---------|-----------------------------|--------------------------|
| Plane (111) | Plane (220) | Plane (211) | Plane (201) | Plane (311) |
| 2:1     | 2.48 | 2.83 | 2.77 | 3 | 3.2 | 3.3 |
| 3:1     | 1.16 | 1.58 | 1.85 | 1.85 | 2.39 | 2.83 |
| 4:1     | 2.17 | 2.39 | 2.5 | 2.83 | 2.62 | 2.77 |

Figure 2 shows the Raman-spectra peak at 520 cm\(^{-1}\) for PS powder and a slight shift to 515 and 513 cm\(^{-1}\), Ni deposition within the pores leads to a further shift of the peak to 505 cm\(^{-1}\) corresponding to the difference in the preparation percentage {Ni: PS = (1:1), (2:1) and (3:1)}, respectively, for the formation of nano-composite (Ni/ PS). Noticeable, at a percentage (4:1), the value of wavenumber increased again to 510 cm\(^{-1}\), as a result of, the complete coverage (saturation case) on a PS surface with Ni-nanoparticles, which is due to compressive stress and then separation of Ni-nanoparticles as reformation of Ni-salt again.
The progress of reducing PS absorbance and increasing Ni absorbance is monitored by UV-Vis spectra which displayed in figure 3.a, b, c, d. That is a direct proportionality between Ni-salt concentration and Ni-nanoparticles absorbance peak intensity, which is adsorbed on PS surface, at a constant deposition time. UV spectra explains very important cyclic behavior, confirmation of the absorbance intensity value for concentration percentage (3:1) at deposition time 30 and 90 min, another confirmation for (1:1) at 60 and 120 min. In addition, the absorbance intensity of Ni/PS nano-composite doesn’t affect with varying the concentration percentages at the deposition time more than 120 min, as shown in figure 3.e.

**Figure 2.** Raman spectrum of (Ni/PS) nano-composite powder chemical deposition process
(a) At different percentage of (Ni:PS), (b) Increasing of NiO spectra at different percentage of (Ni:PS), and (c) Decreasing of PS spectra at different percentage of (Ni:PS).

The PS powder surface {several planes as shown in figure 1} is liable to produce surface Si-H$_2$ and Si-H$_3$. These active Si-H$_x$(x = 1, 2 or 3) species involve in the reduction of Ni(II) while Si-H$_x$ are oxidized into H$_2$. The redox reactions are depicted in the following chemical reaction mechanism. The surface Si-H$_x$ species donate electrons which accepted by Ni(II) bring in gab out manufacture of Ni on PS surface. That means surface Si-H$_x$ bonds play an important role in the reducing Ni(II). The porous architectures of silicon surface which bring vast surface Si-H$_x$ species play vital roles in producing nano particles of a Ni element on PS surface.
Figure 3. UV spectra of (Ni/ PS) nano-composite powder chemical deposition process at different percentage of (Ni: PS) at different deposition time: (a) At 30 min, (b) At 60 min, (c) At 90 min, (d) At 120 min, and (e) At over 120 min.

FTIR measure the change in the PS chemical composition after immersion process in Ni-salt solution and the form of Ni which is deposited on the PS surface. As shown in figure 4, the present peaks of PS after immersion process in Ni-solution are the same as those observed in pure PS. The observed FTIR peaks are located at around 600 to 750 cm$^{-1}$ (wagging modes) associated with Si-H$_n$ ($n \geq 1$) bonding, the band at 1,000 to 1,300 cm$^{-1}$ corresponds to the stretching modes of the Si-O-Si bonds in the PS. The obtained results of PS spectra have not given any indication of the presence of Ni on the PS surface at this stage, no peak corresponding to Ni bonds was observed. Identifies the presence of Ni on PS is appearing in three different percentage spectra {(2:1), (3:1) and (4:1)} with different intensities corresponds to the Ni percent, as shown in figure 4. There appears as a new peak centered at 470 cm$^{-1}$ which is generally attributed to Ni-O bonds [6]. The formation of NiO is an indication that Ni is deposited on PS in its metallic form and not in the form of its oxide (Si-O-Ni). Results of FTIR spectra agree with the above data of different characterization, the (3Ni: 1 PS) is the most suitable percent in the nano-composite preparation technique, which corresponds to the highest value of (Ni-O) peak intensity.
The optical properties of the as-formed hybrid nano-structures were evaluated by measuring the PL spectra [7]. Figure 5.a shows the PL spectra of PS powder at 607 nm (2.04eV). Figure 5.b shows the enhancement of PL intensity after the PS chemical treatment at different percentages of Ni. The PL peak is red shifted at 663 nm (1.87eV). This corresponds to a shift towards the longer wavelength. The enhancement of PL intensity after the Ni nanoparticles deposition process may be attributed to the passivation of surface states in PS in a way that reduces the number of dangling bonds. Under this condition, the closely spaced surface states of PS can act as continuous energy levels and thus transfer the energy to the conduction band of Ni, resulting in emission [7].
Then, we have the very simple chemical technique for preparation nanocomposite (Ni/PS) powder which is used in several fields. That is as a result of the differentiation in PS properties: PS treated with Ni have an enhancement of thermal stability, which is used as a thermal insulator [9]. In addition, it has an enhancement of optical properties as PL spectra which is shown at present work. Nor has there been many differences in PS properties, leading to the use of PS in many applications in several fields.

4. Conclusions
Nano-composite (Ni/PS) powders were prepared using deposition technique of PS powder in an aqueous NiCl$_2$ solution. The properties of the (Ni/PS) powders were systematically investigated as functions of the deposition time and Ni-salt concentration. The Raman spectra analysis indicated that the Ni-content deposited on the PS surface (the PS powder has a large surface area with respect to the Si powder) direct proportionality with increasing the deposition time and Ni salt until arriving to the saturation case, which appeared at (4Ni: 1 PS) percentage. After Ni was deposited, the PS powders changed from hydrophobic to hydrophilic because of the oxidation of the PS surface, as shown in FTIR spectra. The synthesis method used here was based on the fully chemical process; (Ni/PS) is a promise nano-composite for different applications because the simplicity of the preparation method. UV spectra explain very important cyclic behavior, confirmation of the absorbance intensity value. The synthesis of a nano-composite Ni/PS powder from powdered PS has been reported up to date. In this study suggest a possibility of an efficient passivation of (PS) by means of the incorporation of Ni, which induces a spectacular passivation of the silicon nanoparticles in the (PS) structure.

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