The characterisation of nanostructured porous silicon/silver layers via Raman spectroscopy

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Abstract. The investigation of porous silicon/silver nanostructured composite layers (PS/Ag) via Raman spectroscopy technique has been carried out. Interpretation of PS/Ag Raman spectra has been proposed. Data from films acquired by varying anodization time showed a significant shift of a Raman peak primarily located at the frequency expected for monocrystalline silicon towards lower energy. In addition to the single peak a number of low-frequency bands emerged in the Raman spectra of silver-functionalised porous silicon. These effects have been interpreted as due to the influence of functionalizing silver nanoparticles and synthesis parameters on the structure and properties of composite material.

1. Introduction
Porous silicon (PS) and PS-based composite nanostructures are of great interest due to unique properties of such materials including photoluminescence, electroluminescence and the dependence of refraction index on porosity. It is well established that porous silicon is a promising material for a number of applications associated with micro-, nano- and optoelectronics, targeted drug delivery, and gas sensing [1] by virtue of its high specific surface area and extensive capability for surface functionalization. Composite porous silicon – silver materials can also act as a promising substrate for identification and structural characterization of various biological and chemical structures due to the presence of pronounced surface enhanced Raman scattering effect (SERS) [3] caused by collective oscillations in silver nanoparticle electron density. It should be noted that silver-functionalized porous silicon layers can be used in order to implement optical filters for fiber-optic communication systems [2], since the contemporary thin-film filters are expensive due to the necessity of ultra-high vacuum maintaining during the synthesis process.

2. Experimental details
PS layers were obtained with anodization of monocrystalline (111) n-type silicon wafers with resistivity of 4.5 Ω·cm. Pre-treatment of the wafers was performed with volatile liquids (acetone) and ultrasonication for 15 minutes. The anodization process was conducted in an electrochemical cell filled with HF-Isopropyl alcohol-Distilled water solution. Anodization time varied in the range of 0.5 to 40 min. The deposition of silver was carried out from an aqueous solution of silver nitrate in a three-electrode electrochemical cell. The silver chloride electrode was used as the reference electrode. Porous silicon acted as a working electrode. The deposition of silver on the surface of porous silicon samples was performed by applying a potential of 700 mV for one minute.
3. Results and discussion

Raman spectroscopy technique has been extensively used in order to characterize both crystalline and amorphous silicon and silicon based nanostructured materials [4]. Raman shift is equal to 521 cm\(^{-1}\) and 480 cm\(^{-1}\) (transverse optical TO – mode) for crystalline (c-Si) and amorphous (a-Si) samples respectively [3]. Thus, if the structure of a particular sample resembles c-Si and a-Si then the corresponding Raman spectra should be close to those of crystalline and amorphous silicon.

Representative Raman spectra of composite PS/Ag layers depending on anodization time are shown in figure 1(a). Initial porous silicon Raman spectrum is depicted as a reference. It should be noted that the Raman shift of the original sample is 521 cm\(^{-1}\) which is indicative of its monocrystalline structure. It is evident than an increase in anodization time (from 0.5 to 40 min) leads to a shift in position of a Raman peak initially located at 521 cm\(^{-1}\) towards lower energies. In this context according to the confinement model [5] it is assumed that this effect is related to the vibrational confinement caused by the formation of silicon nanocrystallites in the composite material structure due to the deposition of silver nanoparticles. The respective sizes of nanocrystalline silicon clusters (\( L \)) corresponding to a certain Raman shift could be estimated by using equation (1)

\[
\Delta \omega = -A \left( \frac{a}{L} \right)^\gamma,
\]

where \( \Delta \omega \) is the frequency down shift of the sample referring to the c-Si line, \( a = 5.431 \) Å is the lattice constant of Si, \( A = 47.41 \) cm\(^{-1}\) and \( \gamma = 1.44 \) are the parameters describing vibrational confinement for spherical Si nanocrystallites. Calculated sizes of Si clusters are summarized in table 1.

| Silicon matrix anodization time, min | Frequency downshift, cm\(^{-1}\) | Value of nanocrystal size calculated according to (1), Å |
|-------------------------------------|----------------------------|------------------------------------------------------|
| 0.5                                 | 1.4                       | 62.7                                                 |
| 1                                   | 1.4                       | 62.7                                                 |
| 10                                  | 2.3                       | 44.4                                                 |
| 20                                  | 2.3                       | 44.4                                                 |
| 40                                  | 3.3                       | 34.6                                                 |

According to equation (1) an increase in anodization time accompanied by the increase in Raman peak frequency downshift (with respect to the c-Si line) leads to a decrease in silicon nanocrystal sizes. It should be noted that such modification of porous silicon crystalline structure characterized with a downshift of the 521 cm\(^{-1}\) Raman peak is presumably related to an effect of stretching as a result of the deposition of silver nanoparticles inside the pores in the silicon surface.
Figure 1(a, b). (a) PS/Ag Raman spectra (500-550 cm\(^{-1}\)); (b) PS/Ag Raman spectra (60-200 cm\(^{-1}\)).

Figure 1(b) shows Raman spectra of PS/Ag layers in the range of 60 to 200 cm\(^{-1}\). According to [6] the Raman bands at 85 cm\(^{-1}\) and 146 cm\(^{-1}\) have been attributed to silver lattice vibrations. Duval et al. [7] states that Raman spectra of both metal nanoparticles and composite materials based on those contain a low-frequency peak the nature of which is related to the mechanical oscillations of nanoparticles under the influence of incident optical radiation. In order to estimate the dimensions of silver nanoparticles deposited on the PS surface we used Lamb theory [7] for the vibration modes of spherical particles. This particular model accounts for the existence of spheroidal and torsional vibration modes. According to Duval only the lowest-energy modes appear to be active and the frequencies of the lowest-energy spheroidal and torsional modes are virtually equal. This fact is related to the presence of strong coupling between surface vibrational and electronic modes whose energy is close to that of incident photons. Herein by using Lamb theory it is possible to derive an equation for the frequency of the lowest-energy spheroidal mode as (2)

\[ \omega_2 = 0.85 \frac{v_t}{dc}, \]

where \(v_t\) is the transverse sound velocity (\(v_t = 1660\) m/s, a value, averaged on the different directions in the crystal [7]), \(d\) is the diameter of the particle, \(c\) is the speed of light in vacuum, the \(\omega_2\) is the observed peak position. Equation (2) leads to the diameter values of Ag nanoparticles deposited on PS surface of approximately 0.7 nm.

It is worth noting that anodization time of 10 minutes leads to the formation of an optimal morphology of silicon surface thus providing a significant increase in Raman signal intensity (see figure 1(a,b)) probably related to the surface enhanced Raman scattering (SERS) effect [3].

4. Conclusion

The porous silicon matrix structure prior to deposition of functionalizing silver particles is similar to that of monocrystalline silicon. The deposition of silver nanoparticles results in the deformation of silicon lattice, accompanied by the appearance of bands being uncharacteristic for the unmodified porous silicon in the Raman spectra of investigated samples. Also the process of silver deposition on the PS matrix surface results in the formation of silicon nanocrystals, accompanied by a shift of the
peak corresponding to monocry stalline silicon (521 cm\(^{-1}\)) towards lower energy. The calculation of the characteristic dimensions of Si nanocrystals is conducted in accordance with the confinement model [5], depending on anodization time of a silicon matrix. The nature of low-energy Raman bands has been associated with the formation of silver nanoparticles (0.7 nm in diameter) inside the pores on the surface of a silicon matrix. Thus the increase in anodization time of PS leads to a rise in the thickness of the porous layer as well as in the pore diameter.

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