

PHOTOLUMINESCENCE AND INFRARED CHARACTERIZATION OF POROUS SILICON PREPARED BY ELECTROCHEMICAL ETCHING.

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ABSTRACT

Porous silicon thin films were prepared by electrochemical etching of p-type silicon substrates in HF + IPA solutions. A vertical anodisation cell was developed to control the etching procedure with high reproducibility. Thin porous silicon were prepared using substrate resistivities of 0.01, 0.1 and 1 Ω -cm. We changed the anodisation current density from 5 to 20 mA/cm², the etching time was 10 minutes. Photoluminescence (PL) and, infrared spectroscopy were used to characterize the samples. A room temperature intense PL signal located in 650 nm appears in all the samples. As the substrate resistivity is decreased a PL signal shift to high energy regions is detected. The infrared spectra were measured using a FTIR spectrophotometer, sensitive to the infrared region from 4000 to 400 cm⁻¹. After electrochemical etching we observed the presence of silicon crystal modes (Si-Si), SiH_x stretching and Si-O-Si.

INTRODUCTION

Over the past decades silicon has been the basic material in microelectronics. The use of silicon for optoelectronic devices compatible with silicon technology is an important challenge during the last time. However, undoped crystalline Si (c-Si), with its indirect bandgap, shows only weak luminescence in the infrared region. In the last decade a great new interest and optimism revive in the development of such devices for the visible and near infrared range since the discovery of room temperature visible photoluminescence (PL) from porous silicon (PS) [1]. Porous silicon is often characterized by an array of free standing crystalline silicon columns (about 2~50 nm in diameter), and a large surface to volume ratio. However, one of the most interesting aspects of PS is a high efficiency room temperature PL in the visible spectrum usually between 600 nm and 800 nm (2.1 eV to 1.55 eV). A complete review over the physical mechanism of luminescence, formation mechanism and method of fabrication of porous silicon is found in reference [2]. In this work we present photoluminescence and infrared absorption on porous silicon films with peak energy ranging from 1.55 to 2.2 eV, prepared from B doped (100) Si substrates and different anodization current density. Transmission FTIR were used to investigate the substrate resistivity influence on the formation species like SiOSi, O_ySiH_x and SiOH on PS samples.

EXPERIMENT

Thin layers of porous silicon were obtained by anodic etching of Si in hydrofluoric acid. The three kind of substrates were single crystal Si (100) wafers, p-type boron-doped with a resistivity of $\rho_1= 0.01-0.09 \Omega$ -cm, $\rho_2=0.1-0.9 \Omega$ -cm and $\rho_3=1-3 \Omega$ -cm respectively. The electrolyte consisted of a 25 % hydrofluoric-acid-ethanol mixture.

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The anodization reaction was performed for 10 minutes with a dc current density varied from 5 to 20 mA/cm². Samples were washing in ethanol and blown dry in N₂ gas immediately after electrochemical anodization. We checked that all the films luminesce red-orange light to the naked eye under 365 nm ultraviolet light irradiation.

The samples were measured with a FTIR spectrometer, sensitive to the infrared region from 4000 to 400 cm⁻¹, and the contribution of the silicon substrate was subtracted from the spectra of the PS samples. All FTIR spectra were recorded in N₂ atmosphere at room temperature.

RESULTS AND DISCUSSION

In Figure 1 the PL spectra of porous silicon films are shown, which have been obtained using the 488 nm line of the argon ion laser for excitation. PL spectra were not corrected for system response. The PS films exhibited a strong PL emission peak in the red/infrared at about 650 nm (1.9 eV), with a full width at half maximum of ~300 meV.

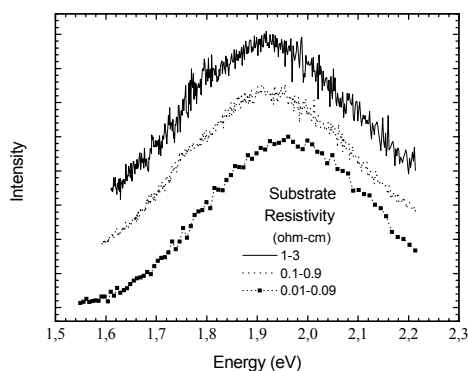


Figure 1: Photoluminescence spectra of the porous silicon films, taken at room temperature as a function of substrate resistivity.

The PL spectra have shown the general trend that the luminescence peak shifts to higher energies as the substrate resistivity are decreased. This result is generally associated with a decrease of silicon crystallite sizes and a variation of the population of non-radiative recombination centers [2,3].

Figure 2 shows IR absorption spectra for samples deposited at different anodization currents on substrates with $\rho_1=0.1-0.9 \Omega\text{-cm}$ and $\rho_2=1-3 \Omega\text{-cm}$ resistivities. It is found that the all spectrum shows a strong absorption peak of about 1060 cm⁻¹ corresponding to the Si-O-Si stretching mode. The peak at 455 cm⁻¹ corresponding to the bond-rocking Si-O-Si modes. The peak at 880 cm⁻¹ can be attributed to the Si-H groups [4]. The range of 1900 to 2300 cm⁻¹ corresponds to the stretching vibrations of the SiH bonds, and has generally been identified as Si monohydride (2090 cm⁻¹), dihydride (2110 cm⁻¹) and trihydride (2140 cm⁻¹) modes [5].

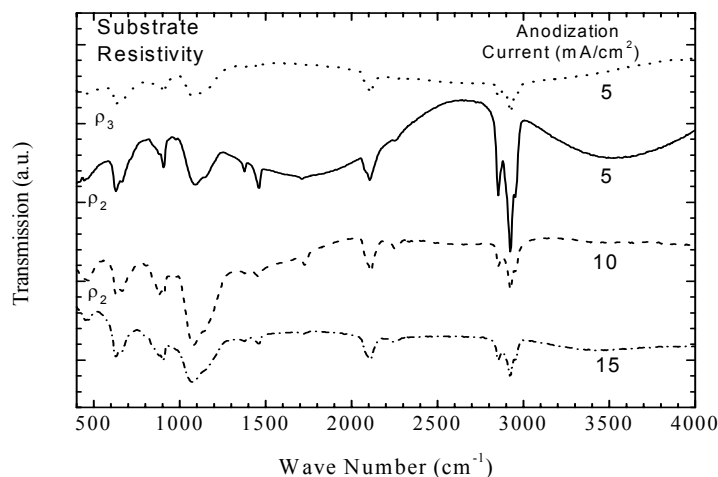


Figure 2: FTIR spectra of porous silicon films deposited on substrates of resistivities $\rho_2 = 0.1-09 \Omega\text{-cm}$ and $\rho_3 = 1-3 \Omega\text{-cm}$, at different anodization currents.

The vibrations around 2950 cm^{-1} can be assigned to a carbon-related vibrational mode. The carbon impurity is originate probably from exposing PS to air which is known to yield some carbon contamination [6], or for the washing in ethanol immediately after electrochemical anodization. The absence of any feature between 3400 and 3600 cm^{-1} , indicates that the OH stretching band is below IR detectable limits. This peak is ascribed to the stretching vibration of SiO-H, and is usually considered to originate from the absorption of water moisture [7]. Comparing the IR spectra of the films in Figure 2, we note that all shows essentially the same IR vibrational features, independent of substrate resistivity or anodization current. From the FTIR results, we noted that hydrides and oxides are the most likely compounds to form in PS films. Furthermore, the FTIR spectra show no significant difference in the chemical composition of samples deposited on substrates with different resistivities o anodization currents. The luminescence may originate from the silicon oxide itself, since SiO_2 is known to luminesce efficiently in the visible under appropriate conditions.

CONCLUSIONS

From the PL measurements and IR spectra is concluded that there is no clear relation between the intensity and peak energy of the PL spectra with respect to the composition of the PS films. We observed a small blue shift of the emission maximum. This result is generally associated with a decrease of silicon crystallite sizes and a variation of the population of non-radiative recombination centers. The second possibility is that the luminescence may originate from the silicon oxide itself. No significant peak shifts were observed in the IR absorptions at the different preparation conditions. The relative

intensities and the positions of the main IR peaks on the porous silicon films prepared in this study are almost the same, indicating that the configuration of the bonding species are similar. No clear correlation between the FTIR spectra information and photoluminescence has been found.

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