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LETTER TO THE EDITOR

Efficient luminescence from CVD diamond film-coated porous silicon

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Received 21 February 2000

Abstract. In this Letter a novel passivation method for porous silicon (PS) surfaces, i.e., depositing diamond film on a PS surface by microwave plasma assisted chemical vapour deposition (MPCVD) method, is reported. The morphologies, structure and PL of CVD diamond film coated PS were characterized using scanning electron microscopy (SEM), Raman spectrum and PL spectroscope. Results indicate that efficient luminescence can be obtained from diamond film coated porous silicon. Also, the CVD diamond film may efficiently stabilize the PL wavelength and intensity of PS, and therefore is a promising candidate for passivation of porous silicon in the future.

In 1990 the visible luminescence of porous silicon (PS) was observed by Canham [1]. Since then the research interest in PS has increased rapidly. However, the major problem of PS luminescence is its poor stability over time [2, 3], mainly due to its changeable surface states. Therefore, to obtain stable luminescence, it is necessary to control the surface states of PS. Many passivation methods, such as anodic oxidation [4] and rapid thermal oxidation [5, 6], have been attempted. Nevertheless these passivation methods always carry the danger of a total oxidation of the PS layer and of transforming it into SiO₂. In this work we attempt to grow diamond films on PS surfaces by microwave plasma assisted chemical vapour deposition (MPCVD) method, aiming to obtain stable luminescence from the PS layers. In the last decade, CVD diamond film is thought to have the combination of a number of favourable properties, such as high hardness, wear heat lash, anti-radiation and transparency to visible light, etc [7, 8].

The PS layers were prepared by conventional electrochemical anodization in a HF-based electrolyte at an electrolytic current of 20–100 mA cm⁻² for 5–20 minutes. The etching was performed on p-Si (111) substrates with resistivities of 2–3 Ω cm. Diamond films, with a thickness of about 0.5 μ m, were then deposited on PS surfaces by MPCVD at 2.45 GHz, the deposition parameters are given in table 1. Figures 1 and 2 present the SEM image and Raman spectrum of a diamond film-coated PS (DFPS) surface, respectively. It was indicated that the homogeneous and dense diamond films could be obtained on PS surfaces using MPCVD

Process	Predeposition	Nucleation	Crystal growth
CH4:H2 (%)	0	5	1
Pressure (Pa)	2000	3000	3000
Substrate temperature (°C)	800	850	870
DC bias (V)	0	-150	0
Depositing time	10min	20min	2hr

Table 1. Typical conditions for the growth of diamond films on porous silicon by MPCVD method.

0953-8984/00/130257+04\$30.00 © 2000 IOP Publishing Ltd

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method. In addition, the characteristic peak of diamond at 1332 cm^{-1} with FWHM of about 11 cm^{-1} was clearly seen, indicating good crystalline quality. The broader band centred at $\sim 1550 \text{ cm}^{-1}$ could be attributed to other carbon species. Crystalline Si was also revealed in the peak at 512 cm^{-1} , being evidence of the desired diamond film transparency.



Figure 1. SEM micrograph of diamond film surface grown on PS.

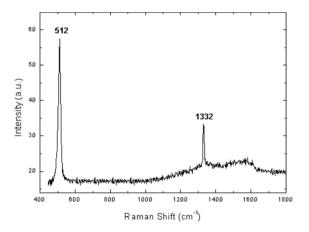


Figure 2. Raman spectrum of the diamond film grown on porous silicon.

Figure 3 presents the PL spectra of fresh PS, stored PS and diamond film-coated PS excited with 360 nm radiation at room temperature, the latter two samples being placed in air for two days. The PL spectrum of fresh PS exhibited a peak at 730 nm, while the peak wavelength of stored PS was markedly shifted towards shorter wavelengths and was at about 680 nm. The shift of emission wavelength was thought to be related both to the break of Si–H bonds and the absorption of O atoms on the PS surface. The PL spectrum of DFPS exhibited two emission bands, a strong red band and a weak blue band. The red band located at 717 nm should originate from the same luminescent centre with relation to the Si–H bonds as in fresh porous silicon. Compared with stored PS without CVD diamond film, the DFPS had a weak

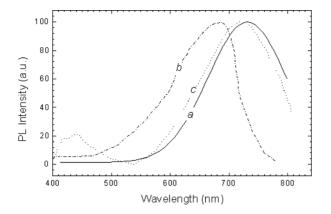


Figure 3. Photoluminescence spectra of fresh PS (a), stored PS (b) and diamond film/PS (c).

shift of emission wavelength, which may be due to the presence of enormous Si–H bonds on the top of PS that were preserved by diamond films. The blue band located at 440 nm is possibly attributed to the band-to-band recombination in silicon nanocrystals. It was obvious that the emission wavelength of porous silicon could be stabilized to a certain degree by the coating of diamond film.

To study the ageing effect, we monitored the luminescence intensity evolution in time by consecutive PL measurements. Figure 4 presents the results of PL measurements for stored PS and DFPS with time. The PL intensity of stored PS without diamond film decreased by 50% after 15 days. However, although the PL intensity of as-grown DFPS decreased by 20% compared to that of fresh PS, there was almost no change with time. Hence it was obvious that the diamond film provided a better passivation effect. The reduction in PL intensity of as-grown DFPS may be due to a graphitic and amorphous carbon layer formation, which are thought to be non-radiative recombination centres, between the PS and the CVD diamond film that may appear during the chemical vapour deposition. Also the different orientations of the diamond micro-crystals at the surface produced some emission dispersion, decreasing the collecting efficiency of the light emission. However, we believe that we can enhance the PL

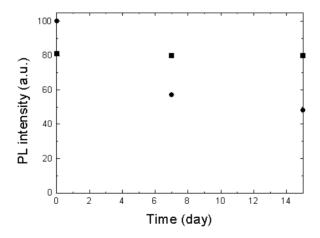


Figure 4. Time evolution of luminescence of stored PS (●) and diamond film/PS (■).

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intensity of as-grown DFPS by optimizing the deposition condition and improving the quality of diamond film on PS, and this work is in progress.

By depositing diamond film by MPCVD on the top of PS surface, we obtained efficient luminescence from diamond film-coated porous silicon. It was clear that CVD diamond film may efficiently stabilize the PL wavelength and intensity of PS. In addition, due to its well known high hardness, diamond film can improve the mechanical strength of PS surface, and is therefore a promising candidate for passivation of porous silicon in the future.

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