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Highly enhanced efficiency and stability of Photo- and Electro- Luminescence of Nano-Crystalline Porous Silicon by High-Pressure Water Vapor Annealing

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1. Introduction

Nanocrystalline Si materials are increasingly important, because of their potential in optoelectronic functions such as visible light emission[1,2] and optical gain[3] effects.

The EL characteristics of nanocrystalline porous Si (PS) have been significantly improved in the past few years. Electrochemical oxidation has led to unprecedented high external quantum efficiencies (EQEs) and power efficiencies of 1.1 % and 0.4 %, respectively [4,5]. The efficiency should be further improved for practical use. In addition, the operation stability needs to be significantly enhanced. The key issue is how to passivate the nanocrystalline Si (nc-Si) surfaces with stable bonds [6].

We propose a treatment based on high-pressure water vapor annealing (HWA) of PS for improvement in both the EQE and stability of the PL and EL. In poly-crystalline Si films, the HWA is very effective to decrease the interfacial trap density at the grain boundaries and to enhance the carrier mobility [7]. It is shown that the HWA drastically improves the PL and EL characteristics of PS. The mechanisms involved in the PL and EL enhancements are also discussed.

2. Experimental

The substrates used for PL studies were (100)-oriented and B-doped p-type (4 Ωcm) silicon wafers. For EL, the same substrates were used, but they were implanted with P atoms (150 keV; dose: 5.10^{15} cm^{-2}) in order to get a superficial n^+ layer of about 500 nm. The PS layers were formed by anodization in ethanoic HF in galvanostatic condition. The layers grown from p-type substrates were formed in dark, whereas layers formed from implanted substrates were formed under illumination, in order to anodize the superficial n^+-type Si layer. The layers were 5 μm-thick.

For HWA treatment, PS samples were heated in water vapor at a temperature of 260 °C for 3 h, and then cooled down to room temperature. The water vapor pressure in the container was 1.3 MPa.

A 200 nm-thick indium tin oxide (ITO) layer was deposited onto the PS layers used for EL investigation. Thus, EL devices consisted in p-Si/p-PS/n^+-PS/ITO junctions. The EL operations were conducted in N_2 atmosphere. The PL measurements were carried out separately by using a 325 nm He-Cd laser as an excitation source.

3. Results and discussion

Figure 1 shows the PL spectra of a PS layer before and after HWA. It can be seen that the PL intensity is very much increased, while the PL emission band is not much changed by HWA. The PL band remains similar to that of conventional luminescent PS in which the luminescence originates from recombination of excitons concerted with surface states [8]. EQE as high as 23 % has been obtained using the HWA treatment. This is much higher than the highest values reported to date (3-4%) [9,10]. Furthermore the PL is very much stabilized by the HWA.

FTIR and ESR measurements have shown that the surface of HWA-treated PS is oxidized and passivated by high-quality (with a very low defect concentration) thin SiO_2 films. The enhancement in EQE and stability is then attributed to a drastic reduction of the rate of non-radiative recombinations and an efficient protection of Si nanocrystals against further oxidation.

These highly luminescent and stable PS layers have been used in order to get enhanced EL characteristics. **Figure 2** shows the EL intensity and the current density as a function of the voltage for (i) a device including a HWA-treated PS layer, and (ii) a device including the same PS layer but untreated. The current flows under forward bias as well as under reverse bias due to the presence of the highly-doped n-type superficial PS layer. The characteristics of the treated device are much better than that of an untreated device with a limited EL emission even at much higher current densities. The current density is reduced because of surface oxidation during the HWA. Obviously the higher EL emission and EQE is due to the high luminescence efficiency of the HWA-treated PS.

Figure 3 shows the EL intensity as a function of time for the treated device. After an initial aging where both the current density and the EL intensity increase, the device becomes very stable, as expected from PL data. In contrast, non-treated device exhibited very poor stability: both the driving current and EL intensity only significantly deteriorates during operation.

4. Conclusions

The HWA improves drastically the PL EQE and stability of appropriately produced PS. A record PL EQE of 23% was obtained. Both the PL and EL exhibit very high stability. The HWA method enables almost complete passivation of nc-Si surfaces with high-quality thin oxides. It is a very practical and promising low temperature approach for producing highly efficient and stable luminescent nc-Si materials and devices.

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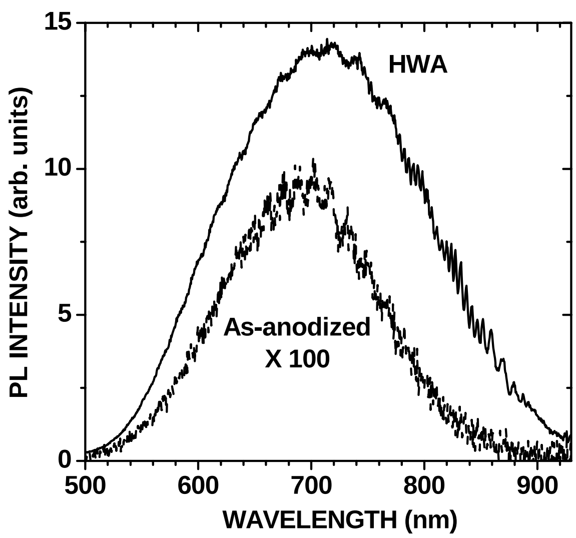

Fig. 1. PL spectra of a PS layer before and after HWA. The HWA was performed at 260 °C for 3 h at 1.3 MPa.

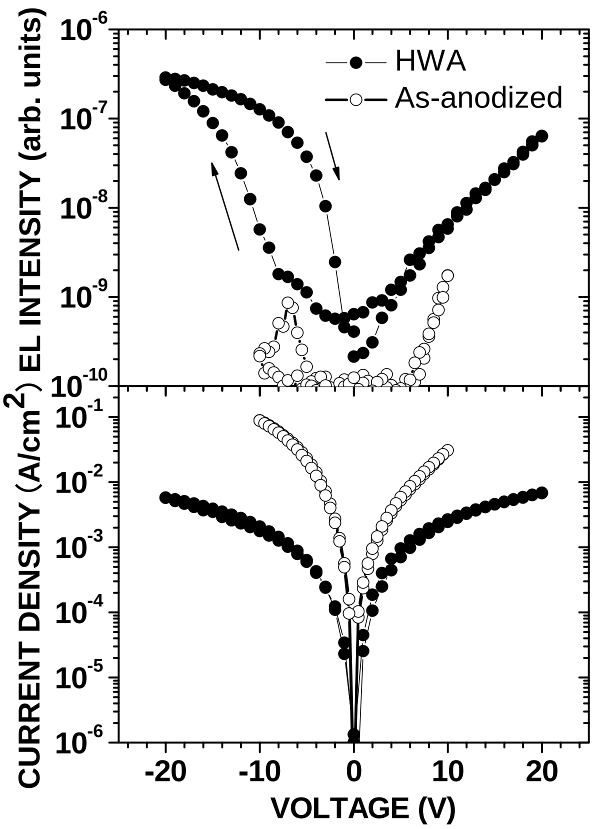

Fig. 2. EL intensity and current density as a function of the aplied voltage for two EL devices with as-anodized PS layer and HWA-treated one.

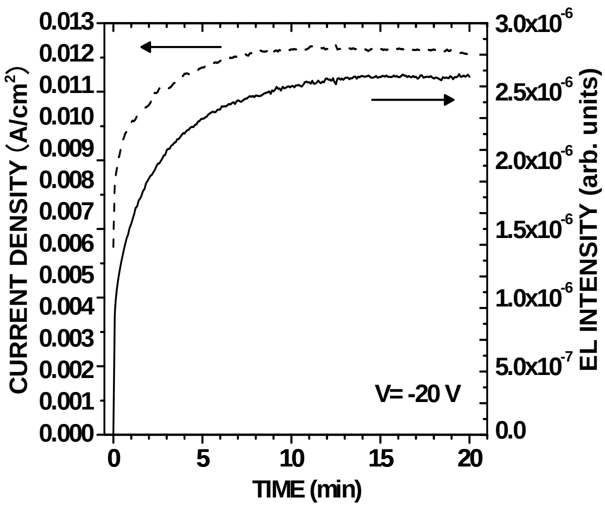

Fig. 3. EL intensity and current density as a function of operation time for the device with a HWA-treated PS layer shown in Fig. 2. The applied voltage was -20 V.