

Photoluminescence and structure properties from $\mu\text{c-Si:H}$ and $\mu\text{c-Si:H-PS}$ samples

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Abstract

Microcrystalline and porous on microcrystalline silicon thin films were produced. The photoluminescence characteristics of porous on microcrystalline silicon were studied and compared with those from microcrystalline and porous silicon grown on silicon wafers. Under steady state it is possible to excite these samples with visible light at room temperature. This excitation gives rise to a red photoluminescence band, which is similar to that of porous silicon excited under the same conditions. MicroRaman and transmission spectroscopy shows that the porous silicon layer was produced below the microcrystalline silicon thin film that acts as a shield for excitation and emission of radiation with a wavelength smaller than 500 nm. Sample thickness, crystallite size and crystalline fraction are determined. The results are discussed in terms of the theoretical framework based in the fluctuating quantum wire model for porous silicon. © 1997 Elsevier Science S.A.

Keywords: Photoluminescence; Properties; Porous silicon; Microcrystalline silicon

1. Introduction

Recently, industry has focused its interest on microcrystalline silicon ($\mu\text{c-Si:H}$). It has the same low temperature preparation as amorphous silicon (a-Si:H) combined with a much higher conductivity than a-Si:H and a higher absorption coefficient than c-Si in the range of visible light. This makes it a much more profitable material for use in solar cells, thin film transistors and light emitting diodes.

Porous silicon (PS), either made anodically [1,2] or by stain etch [3], is a novel material with a broad luminescence band visible at room temperature [4] being a promising material to construct new devices, especially in the optoelectronics field.

Integrating both materials, the proprieties of $\mu\text{c-Si:H}$ can be enhanced, since we can have a device emitting in the visible range giving the possibility of operating also as a source.

In this work we studied this integration producing porous on microcrystalline silicon ($\mu\text{c-Si:H-PS}$). Its photoluminescence (PL) and microRaman (μR) response are compared with those from $\mu\text{c-Si:H}$ and PS for different excitation wavelengths. The results are made constant with the “fluctuating quantum wire” model of PS [5].

2. Experimental details

All samples used in this work were grown on p-type, 5 Ω cm, [100] Si monocrystalline wafers. $\mu\text{c-Si:H}$ samples were produced placing the target substrates into a Alcatel SCM 650 sputtering machine, using a radio frequency (RF) of 13.56 MHz with a power of 150 W. Reactive sputtering deposition was performed after reaching a base pressure of 2×10^{-4} Pa. The sputtering target was a hyperpure Si wafer spaced 60 mm from the substrates. To deposit the films, the target was bombarded by a 7.5 cm diameter “unbalanced” magnetron. The samples were grown using gas pressures of 0.34 Pa for H_2 and 0.23 Pa for Ar.

$\mu\text{c-Si:H-PS}$ and PS samples were prepared by electrochemical etch in hydrofluoric acid, 50 wt.%, under anodisation, using natural illumination and a platinum wire as counter electrode. Two sets of samples were produced with different current density: one with 13 mA cm^{-2} and other with 25 mA cm^{-2} , both during 1200 s.

PL spectra were obtained with two exciting sources: an ultra-violet continuous wave (CW) laser, tuned at 364 nm, and a tungsten (W) lamp with an output power approximately constant between 600 nm and 800 nm in our system. At the sample surface the maximum power of the W lamp, after focusing, was 10 mW, while the laser was set to 80 mW. The spectra were acquired using a spectrometer, SPEX 1704, and a water cooled photomultiplier tube.

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The μR system consists of a 15 mW He–Ne CW laser tuned at 632.8 nm mounted in a Raman Imaging Microscope System 2000 (Renishaw). The system incorporates a simple monochromator. There is a spatial resolution of 1 μm and a spectral resolution of 1 cm^{-1} . The radiation is collected by a CCD camera.

All spectra were obtained at room temperature, corrected for spectral response of the detection system and analysed by hardware equipped with original software.

3. Results

Optical transmission and reflection measurements allow to determine the thickness of the $\mu\text{c-Si:H}$ layer ($d \approx 1760$ nm). After etching the samples, this layer becomes approximately 0.4 times thinner. The data were calculated according to procedures proposed by Minkov [6] and Swanepoel [7].

$\mu\text{c-Si:H}$ and $\mu\text{c-Si:H-PS}$ have a μR spectra similar to c-Si [8] for a Raman shift below 1000 cm^{-1} . The main peak of c-Si (520 cm^{-1}) appears shifted from its position owing to the finite size of the crystals and to the stress in the film. We also point out the presence of hydrogen in the samples detected by the presence of a 2150 cm^{-1} μR peak [9]. These contributions can be seen in the typical μR spectra shown in Fig. 1.

The deconvolution of these spectra in the range from 350 cm^{-1} to 600 cm^{-1} reveals three Lorentzian unshaped peaks between the frequencies of a-Si (480 cm^{-1}) [9] and c-Si (520 cm^{-1}). The peak between 495 cm^{-1} and 520 cm^{-1} is related to the crystalline phase. The position of this peak is directly related to the grain size. The broad peak at approximately 480 cm^{-1} is related to the amorphous phase. A relatively important peak at about 490 cm^{-1} is frequently found in Si thin films with very small crystals owing to the near-surface region [10,11]. To determine the crystalline volume fraction, C [12], we use

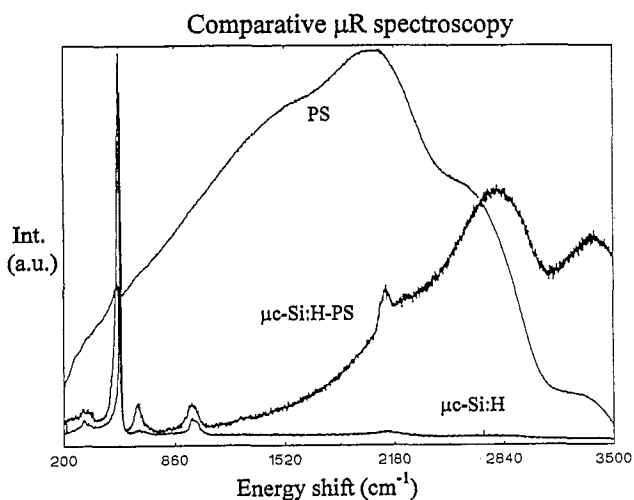


Fig. 1. μR spectra from $\mu\text{c-Si:H-PS}$ and PS. c-Si phonons can be seen together with Si–H bonds for $\mu\text{c-Si:H-PS}$. In PS only the TO phonon is perceptible in the left side of the luminescence band.

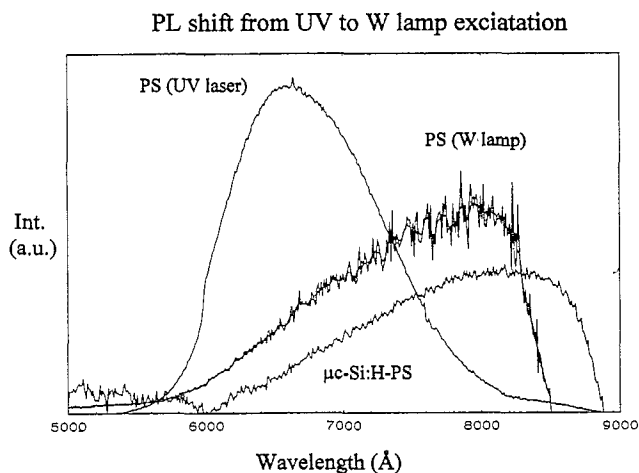


Fig. 2. PL spectra from PS and $\mu\text{c-Si:H-PS}$ samples at room temperature with different excitation: UV laser and W lamp for PS and W lamp for $\mu\text{c-Si:H-PS}$.

$$C = \frac{I_c}{I_c + I_a(0.1 + e^{-S/25})}$$

where I_c is the integrated intensity of the two crystalline components, I_a the integrated intensity of the amorphous peak, S the size of the crystallites and 25 is expressed in nm. For C it was found 56% to $\mu\text{c-Si:H}$ and 47% to $\mu\text{c-Si:H-PS}$. S , the average size of the crystallites has also to be taken into account since it can influence the value for the scattering cross-section. We determined that S equals 27.7 Å before chemical attack ($\mu\text{c-Si:H}$) and 15 Å afterwards ($\mu\text{c-Si:H-PS}$).

PS samples grown on crystalline Si wafers have a PL band in the visible region, when excited with UV, as can be seen in Fig. 2. When excitation wavelength is changed from UV laser to W lamp, the PL band of PS shifts to red.

We found that porous on microcrystalline silicon samples cannot be excited with UV radiation as PS, but only with a W lamp showing a red PL band similar to the one of PS. No preferential exciting wavelength was detected for the PL of $\mu\text{c-Si:H-PS}$ in the range from 550 to 800 nm.

$\mu\text{c-Si:H}$ shows no visible PL at room temperature when excited in the same conditions as $\mu\text{c-Si:H-PS}$ or PS.

μR spectra became fundamental in sample analysis because the photomultiplier has a cut off in the near infrared region. From Fig. 1 we can see that μR spectra for the different samples studied is superimposed on a broad luminescence band. As can be seen, this band is more structured and has the stronger contribution from the TO mode of a-Si for $\mu\text{c-Si:H-PS}$. Only $\mu\text{c-Si:H}$ based samples present a clear μR peak at 2150 cm^{-1} corresponding to Si–H bonds [9].

4. Discussion

When PS is grown on $\mu\text{c-Si:H}$ the microcrystalline layer is attacked by HF. The thickness of the layer and the size of

the micro-particles decreases and the refractive index changes. Owing to the crystal interfaces and surrounding amorphous phase the chemical attack in $\mu\text{c-Si:H}$ is easier than in c-Si. A good control of the production time is important in order to prevent the complete dissolution of the $\mu\text{c-Si:H}$ layer.

$\mu\text{c-Si:H}$ has a strong absorption below 500 nm [13] and works as a shield to UV excitation but not to W lamp (yellow) excitation. So we conclude that the porous layer is grown underneath a thin $\mu\text{c-Si:H}$ coating. This is the reason why UV light cannot excite the $\mu\text{c-Si:H-PS}$ layer as observed experimentally.

The presence of hydrogen in spectra of $\mu\text{c-Si:H-PS}$ is clearly seen from μR (Fig. 1), supporting the evidence of a residual $\mu\text{c-Si:H}$ layer. However, hydrogen does not seem to play a fundamental role in the red emission band of $\mu\text{c-Si:H-PS}$ samples since this band is very similar to the PS red band as shown in Fig. 2.

UV excitation is sufficiently energetic to excite PS pairs above its maximum band gap height resulting in a broad orange band composed of a red and a blue component [5]. Changing the excitation from UV to yellow light we cannot excite the pairs above the maximum height of the gap, leaving the more energetic sites unoccupied. In this way, only pairs of low energy can recombine and the luminescence from $\mu\text{c-Si:H-PS}$ and PS samples shows the red component [5,14].

5. Conclusions

In this work it was shown that the microcrystalline silicon, integrated with porous silicon, becomes a material with a larger potential for practical applications owing to the possibility of having, in the same sample, high surface conductivity and absorption coefficient together with a good visible emission, not possible without this integration.

The residual microcrystalline silicon layer on $\mu\text{c-Si:H-PS}$ works as a shield for radiation with wavelength below the transmittance edge of microcrystalline silicon and inhibits the blue component of porous silicon emission band.

In principal, devices can be produced taking advantage of the peculiar characteristics of this material.

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