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Fabrication and Optical Characterization of Self-standing Wide-gap Nanocrystalline Silicon Layers

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1. Introduction

Nanocrystalline silicon is today one of the most promising and researched material for its potential applications as electro-luminescent display, ballistic electrons and ultra-sounds emitter, various photonic devices and more recently solar cells. To indicate the availability of such wide-gap nanocrystalline silicon layers to use as a top cell for silicon-based multi-junction photovoltaic devices, the fabrication technology of self-standing nanocrystalline silicon layers has been developed. The outline of the process flow is presented in this abstract as well as different passivation treatments and their effects on the optical characteristics of nanocrystalline silicon.

2. Experiments

Self-standing nanocrystalline silicon layers (nc-Si) were prepared from (100) oriented boron doped p-type (2.4-3.6 Ω.cm) single-crystal silicon. As shown in **Fig. 1**, the technique employed here is based on the standard wet processing termed anodization. At first, the single-crystalline silicon surface is electrochemically etched in an HF solution (55% HF: Ethanol = 1:1) at a moderate current density to produce a uniform porous silicon layer composed of nanocrystalline silicon dots (Porosity around 68%). When the depth of the anodized layer reaches a certain value (estimated from the experimental parameters, 35μm in this study), the anodization current is rapidly increased up to a current level of electro-polishing mode (around 500mA/cm^2), and then the nc-Si layer is peeled out from the substrate.

To stabilize the surface termination, the self-standing samples are then treated by different thermal treatments such as rapid thermal oxidation (RTO) and/or high pressure water vapor annealing (HWA). RTO was conducted in a temperature range of 300–900ºC under a constant O_2 flow during approximately 60min. The samples were also treated by HWA by placing them in a closed metallic container with de-ionized water and then were heated at 260ºC during 3 hours. The water vapor pressure during annealing was adjusted to 2.6MPa.

The optical characterization of the resulting samples were done by measurements of optical transmission and absorption using a spectrophotometer Hitachi U-4100, measurement of photoluminescence at room temperature using a 325nm He-Cd laser and finally polarization memory and PL dynamics.

3. Results and discussion

- Effect of oxidation on photoluminescence

Fig.2 shows the PL spectra of a sample after anodization, RTO treatment and a combination of RTO and HWA. As expected from nano-crystalline silicon, the PL spectra of samples after anodization are in the red band (peak at 830 nm). For the combination of RTO and HWA, their effects have been discussed in a previous publication[1]. Oxidation by RTO at high temperature lead to a PL spectrum with two different peaks clearly visible: the conventional red band from nano-crystalline silicon and a new band in the blue region which may be caused by localized states in Si oxide or originate from the silicon-oxide interface. In our samples, the blue and red bands coexist due to the fact that the porous silicon may be not sufficiently oxidized yet. After HWA treatment, we can see a drastic enhancement of the blue band intensity. While after RTO the blue and red bands have a nearly equivalent intensity, after RTO and HWA the blue band emission is clearly dominant, confirming that the HWA treatment is a useful technique to obtain stable and efficient short wavelength PL emission.

- Optical Transmission and absorption

Due to the porous nature of the material and the thickness of the self-standing layers, the color of the as-anodized samples is semi-transparent dark red (35μm thick samples). After a first RTO treatment, the optical properties are clearly modified by the heavy oxidation of the nc-Si material. As seen in **Fig.3**, blueshift of the absorption is visible after anodization and even more after oxidation from RTO and HWA, indicating a widening of the band-gap due to quantum confinement in Si nano-dots. While HWA applied after RTO does have an important impact on short wavelength PL, effects on the optical absorption remain negligible as samples treated with RTO and HWA have a similar absorption spectrum than that treated with RTO only.

- Polarization memory and PL dynamic response

Polarization memory (PM) measurements have been used to analyze and compare the red and blue emission separately[2]. PM of the red band is anisotropic, a characteristic in agreement with emission from Silicon nanocrystals themselves while the blue band shows a PM that is clearly isotropic, suggesting that the origin of the emission is different from the red emission and may be related to localized states in the Si oxide. Moreover, PL dynamic response measured at room temperature shown in **Fig.4** presents a decay time of around 120µs for the red band (600nm) and a long decay of 1.5s for the blue band (440nm) not observed in conventional Si-based materials, suggesting that luminescence at high energy proceeds from a different mechanism than red fluorescence.

4. Conclusion

We have confirmed the possibility of fabricating self-standing nc-Si layers with various thicknesses and applied different oxidation treatments successfully. The measured photonic properties of prepared layers feature interesting characteristics which could lead to potential application as a top cell for silicon-based multi-junction photovoltaic devices.

Acknowledgements

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References

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[2] B. Gelloz, H. Koyama, N. Koshida. Thin Solid Films 517 (2008) 376-379

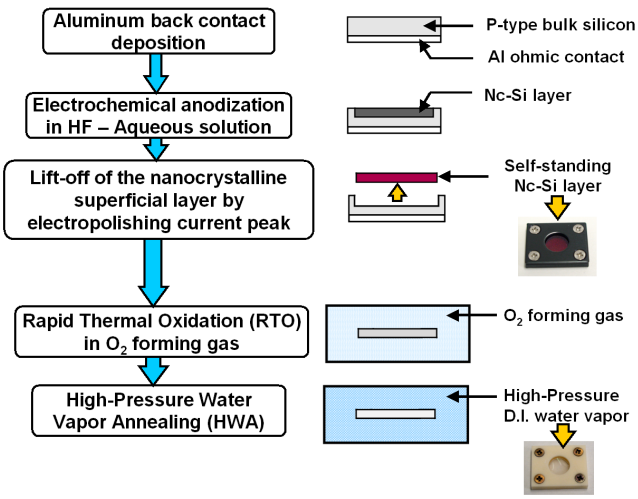

Fig. 1. Process flow for the fabrication of self-standing nc-Si layers and oxidizing post-treatments. Resulting samples are shown mounted in special metallic and ceramic holder.

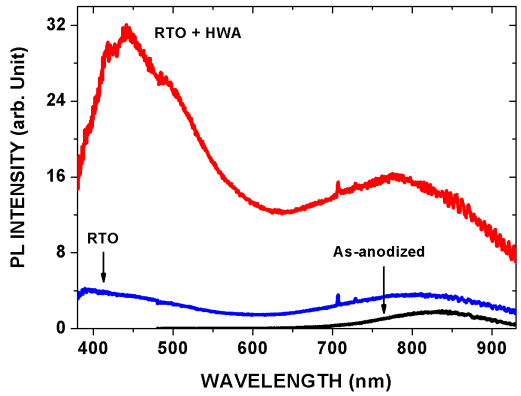

Fig. 2. PL spectra of self-standing as-anodized nc-Si layers of 68% porosity, after RTO and after RTO + HWA.

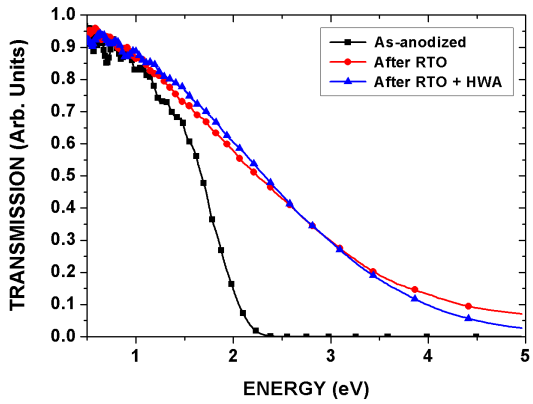

Fig. 3. Spectral dependence of the optical transmission for as-anodized self-standing nc-Si layers before and after RTO / RTO + HWA.

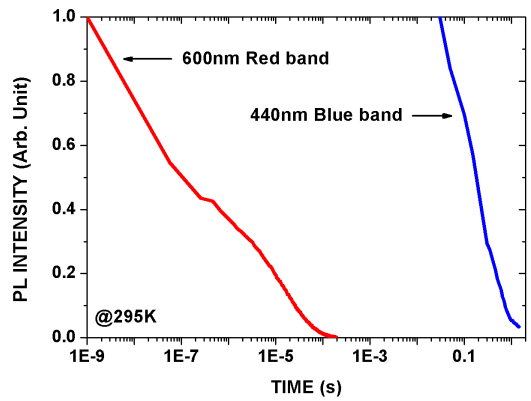

Fig. 4. Room temperature PL decay for the red and blue band vs. logarithmic time in second (due to orders of magnitude between the two PL response times).