NANOSTRUCTURAL STUDY OF LUMINESCENT POROUS POLYCRYSTALLINE SILICON

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ABSTRACT

Luminescent porous poly-Si films with large areas or micron-sized patterns have been obtained by anodization or stain etching of phosphorus-doped poly-Si films deposited by low pressure chemical vapor deposition onto Si, thermal oxide or CVD nitride. The anodized film is composed of spherical Si grains with nano-pores formed around the surface. However, the stain-etched film has large rectangular Si grains, and no nano-pores can be observed. The intensity of photoluminescence is enhanced after nitric acid boiling or stain etching, and is found to be closely related to the crystallinity of the porous Si layers.

INTRODUCTION

Efficient light emission from porous silicon (Si) has drawn considerable interest since it was first reported by Canham¹. Recently, visible photoluminescence (PL) has also been found to be emitted from porous Si (PS) layers formed by anodized or stain-etched polycrystalline Si (poly-Si)²⁻¹¹. The new luminescent porous poly-Si (PPS) film can be formed on Si or non-Si substrates such as oxide, metal or glass, and hence has numerous novel practical applications in future Si-based opto-electronic devices, such as sensors, photodetectors and displays. The study of PPS can also help engineers to understand and control the mechanisms for light emission from Si, as poly-Si of various crystallinities and grain sizes can be prepared. However, until now little research has been done on this important material. In this article, we present the results of our nanostructural and PL study of anodized and stain-etched PPS films formed on different substrates.

EXPERIMENT

Undoped poly-Si thin films with a thickness of 670 nm were deposited onto <100> 5-10 Ω -cm p-type crystalline-Si (c-Si) substrates. Poly-Si films of around 450 nm in thickness were also deposited onto 95 nm-thick thermal oxide or 200 nm-thick low pressure chemical vapor deposition (LPCVD) nitride layers formed on Si substrates. The poly-Si films were formed by thermal decomposition of silane gas (SiH_4) in a LPCVD reactor at 625°C for 50 min. The flow rate and pressure of silane were 150 sccm and 300 mTorr, respectively, and the poly-Si deposition rate was 10 nm/min. Phosphorus was then diffused into the samples at 950°C for 20 min to form 12 Ω /sq n-type poly-Si films. Micron-size patterns were also defined on some poly-Si films using reactive ion etching. To form the PPS layers, poly-Si films were anodized in dilute HF solution (49%HF:ethanol ($\text{C}_2\text{H}_5\text{OH}$)=1:1) with a Pt electrode at a current density of 10 mA/cm^2 for 5-10 min in room light and at room temperature. P-Si substrates were also anodized under the same conditions for comparison. Poly-Si films were also stain etched in HF: HNO_3 :DI 1:3:5 solution for 0.5-2 min in room light and at room temperature. The incubation time for the stain-etched PPS film was about 20-30 sec. For passivation tests, some PPS samples were

further boiled in nitric acid (HNO_3) for 5-10 min. The poly-Si and PPS films were then studied using a Jeol 6300F scanning electron microscope (SEM) and a TopoMetrix TMX 2000 atomic force microscope (AFM). PL spectra were studied using a SPEX 1403 PL Spectrometer with Innova 400 nm uv laser excitation. X-ray diffraction (XRD) was studied using a Philips PW 1710 system.

RESULTS AND DISCUSSION

AFM and SEM study

From the AFM micrographs, the submicron poly-Si films are smooth (roughness ~ 30 nm) and the poly-Si grains are uniformly distributed in the film. The sizes of the grains are almost spherical with a diameter of about 150 nm (Fig. 1a). After 5 min of anodization, the PPS films formed are found to retain similar roughness and grain structures as the original poly-Si layer (Fig. 1b). The film is composed of Si grains (about 150 nm in size) with numerous nano-pores (about 20 nm in size) formed around the surfaces of the grains. Similar roughnesses, nano-pores (~ 20 nm) and nanostructures have also been observed in high-resolution SEM surface micrographs and AFM contour micrographs. Contrarily, stain-etched PPS films are found to have rectangular grain (~ 150 nm) nanostructures. The grains group together to form larger blocks (~ 0.5 - 1.5 μm) and no nano-pores are found (Fig. 1c). Similar nanostructures have also been observed in high resolution SEM micrographs. The rectangular blocks may be due to the increased oxide formation around the PPS grain surfaces and the nanostructure is different from those of the stain etched PPS films in other works^{6,10}. To the best of our knowledge, this is the highest resolution AFM and SEM report on stain-etched PPS film. Furthermore, from the cross-sectional SEM micrograph, an anodized PS layer is formed from the c-Si substrate below the anodized PPS film and its thickness is about 100-200 nm (Fig. 1d). The PS layer shows a similar grain-like nanostructure to the PPS film and that is different from the wire-like nanostructure usually reported in other works.

To explain the new AFM and SEM results, we propose the following model for the growth mechanisms and nanostructure formations for our PPS films. For anodized PPS films, anodization current flows along the $\langle 100 \rangle$ Si crystallographic direction in the Si substrate. At the poly-Si and Si substrate interface, the current mainly flows along the poly-Si grain boundaries due to the preferential dopant diffusion and lower resistance. In our samples, as the size of poly-Si grain was only about 150 nm and the grain density was high, the current can be assumed to have flowed uniformly around the whole grain surface. Hence, the grain was uniformly anodized and became a macro-grain with many nano-pores formed around the surface after the anodization. The etching of grains and formation of PPS film is analogous to the etching of a coral-ball layer due to sea water. At the c-Si and poly-Si boundary, current mainly flows along the grain boundaries and hence the etching of c-Si and poly-Si film is similar, causing similar nanostructures for the anodized PS and PPS layers.

PL emission

The poly-Si films show no PL under ultra-violet light excitation. The results agree with the other reported works². After 5 min of anodization, PPS films emit uniform orange-red PL. The PL intensity is uniform and weak, and increases slightly with the anodization time and current density. A similar result has also been reported by Guyader et al.² After 10 min of post-anodization HNO_3 boiling, the PL of the PPS films is found to be enhanced. Similar strong PL is also found in stain-etched (0.5-2 min) PPS films formed on Si substrates, thermal oxide or LPCVD nitride. PL enhancement after nitric acid treatment has already been reported in PS films

formed in anodized Si¹², and our results may also be due to the nitric acid present in the stain etch and the nitric acid passivation solutions. We believe that ours is the first report on PL enhancement from PPS films and details of the results will be published elsewhere.

Figure 2 shows the typical PL emission spectrum for the new PPS films. The peak of PL is about 690 nm and full wave half maximum (FWHM) is about 100 nm. The peak PL is longer than the results reported for other PPS films (640-690 nm) while the FWHM is shorter (110-195 nm)^{2-6,9}. The PL spectrum of the PPS film is also found to be highly comparable to that of the PS film formed from same p-Si substrate anodized under the same conditions. This suggests that though the PS and PPS films show quite different surface and pore nanostructures, they may have similar light emitting centers. Our results also agree with the previous works that PPS and PS have similar PL^{2,3,6}. Uniform PL is also found from anodized PPS films with both large areas and micron-sized patterns.

Figure 3 shows the SEM micrograph of a typical micron-sized pattern. The width of the PPS line is about 2 μm . The grains are closely packed and uniformly distributed, and the size of the grains is about 150 nm which is in good agreement with the AFM and SEM results. Ours result is the first report of PL emission from anodized micron-size PPS thin film, though stain-etched PPS micron-sized thin film has been reported⁶. These PL results can be used to develop new methods to produce light emitting micron-sized Si thin film devices, which will have numerous revolutionary applications in very large scale integrated electronics. Compared to stain etching which basically uses etching time to control the PPS layer formation, anodization has the advantage of an extra current control, despite the drawback of a more complicated sample preparation process.

XRD and crystallinity

Figure 4 shows the XRD spectra and the integrated intensities of the c-Si peaks for the PPS films with no PL, weak PL and strong PL. Both the anodized and stain-etched PPS films have the same XRD c-Si peaks. For the poly-Si and PPS films which have no PL, the XRD spectra show mainly (220), (111) and (200) c-Si peaks (planes). However, PPS films with weak PL show only (200) and (220) c-Si peaks and no (111) peak is found. The (200) peak intensity is reduced after 5 min of anodization but much enhanced after 10 min of anodization. For PPS films with strong PL, only a weak (200) XRD c-Si peak or no peak is found. PPS films may also have a (400) peak but the signal is mixed with the (400) c-Si peak signal from the <100> Si substrate. Double peaks at (200) and (400) planes are also observed and are due to the α_1 and α_2 wavelengths of the x-ray source. Besides the major (220), (200) and (111) XRD c-Si peaks, very weak (110) and (311) peaks are also observed from the PPS films.

The XRD c-Si peaks suggest that the poly-Si and PPS films are partially crystallized. The grains are parallel to the surface and consist mainly of crystallites oriented in the <111>, <220> and <200> directions (with (220), (111) and (200) planes). Assuming that PL emission is due to nano-Si crystallites as proposed by many porous Si theories, increases in etching may cause the formation of more nanocrystallites and hence stronger PL. Moreover, etching may mainly occur in the (111) (and (220)) planes, hence stronger PL is found in PPS samples with (200) (and (200) and (220)) c-Si planes. Our XRD results are also different from the previous works. In the work of Ueno and co-workers⁵, cast poly-Si films underwent no significant change in XRD after anodization. In the work of Steckl et al.¹⁰, LPCVD films deposited at >590°C were increasingly polycrystalline with a <220> orientation, and with weak peaks at <111> and <311>. After stain etching, the <220> peak was still present but with much weaker intensity. In the work of Bustarret et al.¹¹, <111>, <220> and <311> peaks were found in PECVD poly-Si films, but no peak could be resolved after anodization.

CONCLUSIONS

In summary, we obtained new results with respect to the nanostructures, photoluminescence and crystallinity in porous poly-Si films formed by anodization or stain etching of phosphorus-doped poly-Si films deposited by low pressure chemical vapor deposition onto different substrates. The light emission may be related to both the Si nano-crystallites and oxide, and a coral-ball analogy model is proposed to describe the etching process and porous Si formation.

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Fig. 1 AFM surface micrograph of (a) poly-Si layer, (b) anodized PPS layer, (c) stain-etched PPS layer, (d) SEM cross-sectional micrograph of anodized PPS layer. White layers at surface are due to sample preparation.

Fig. 2: Typical PL emission spectrum of the PPS films. Y axis is intensity in arbitrary unit.

Fig. 3. SEM micrograph of luminescent micron-sized anodized PPS film pattern

Figure 4: XRD spectra of the poly-Si and PPS films.
(a) no PL, (b) weak PL, (c) (d) strong PL. Y-axis is intensity in arbitrary unit.