Photoluminescence from stain-etched polycrystalline Si thin films

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Visible room-temperature photoluminescence (PL) has been observed from stain-etched polycrystalline Si thin films. Poly-Si thin films deposited on oxidized Si and quartz substrates became porous (PoSi) after stain-etching in a 1:3:5 solution of $HF:HNO_3:H_2O$. Under UV excitation, the stain-etched doped and undoped poly-Si films produce uniform orange-red ($\sim$650 nm) luminescence very similar to that obtained from stain-etched crystalline Si substrates. Stained amorphous thin films did not exhibit photoluminescence. Luminescent patterns with sub-micrometer ($\sim$0.6 μm) dimensions have been obtained for the first time from PoSi produced from poly-Si films.

Visible, room temperature photoluminescence (PL) has been previously reported from crystalline Si (*c*-Si) which has been anodized[1,2] or stain-etched[3,4] to form a porous Si (PoSi) layer. PL from hydrogenated polycrystalline Si (poly-Si) treated with two electrochemical processes was recently reported.[5] In this letter, we present the first report of visible PL from stain-etched, initially polycrystalline Si (poly-Si). Undoped amorphous and poly-Si films of around 400 nm were deposited on oxidized Si substrates by low-pressure (180 mTorr) chemical vapor deposition (LPCVD) from SiH_4 at 560 and 600 °C, respectively. The poly-Si films grown at 600 °C had a sheet resistance (R_{sh}) of $\sim$1–10 MΩ/sq. Doped poly-Si films were produced by 30 kV P^+ ion implantation of the amorphous films grown at 560 °C and followed by annealing at 900 °C for 30 min yielding an $R_{sh}\approx 20$ Ω/sq. Thicker (2 μm) undoped poly-Si films were also deposited on quartz substrates at 630 °C.

The poly-Si films were stain-etched in a 1:3:5 solution of $HF:HNO_3:H_2O$ at 25 °C in ambient light. The incubation times (t_i) for PoSi formation were uniformly small, 10–20 s, for both doped and undoped poly-Si films. This is in contrast to the strong effect of the doping (hole) concentration observed[6] on the t_i for stain-etching of *c*-Si. Total stain etching times for the poly-Si films on SiO_2/Si and on quartz were 30 and 120 s, respectively. The surface morphologies of the doped and undoped poly-Si films on oxidized Si are shown before and after stain-etching in the SEM microphotographs of Fig. 1. The as-received doped poly-Si film has a relatively smooth surface [Figs. 1(a) and 1(b)], since it was amorphous as-grown and only became polycrystalline upon anneal. A slight surface texture can be observed in the tilt-view microphotograph [Fig. 1(b)]. The undoped poly-Si film exhibited a grainy surface in the as-received condition [Figs. 1(c) and 1(d)] with a typical grain size of $\sim$0.1 μm. The stain-etching process clearly reveals grains with $\sim$0.2–0.4 and 0.1–0.2 μm average dimensions in the doped [Figs. 1(e) and 1(f)] and undoped [Figs. 1(g) and 1(h)] poly-Si films, respectively. The surface texture is considerably rougher after stain-etching for both doped and undoped films.

Atomic force microscopy (AFM) of the poly-Si surface was used to provide a quantitative measure of the surface roughness (R_a). For the doped film, R_a before and after stain-etching was 1.89 and 18.0 nm, respectively. As expected, the undoped film exhibited a rougher as-deposited surface with a R_a of 5.65 nm. However, after stain-etching, the roughness of the undoped (18.53 nm) and doped (18 nm) films was essentially the same.

PL spectra were obtained with ultraviolet (UV) excitation at 370–380 nm from a filtered Hg source. The emission from poly-Si layers on oxidized Si substrates, shown in Fig. 2, exhibits a broad signal with a peak at 640–645 nm. No significant difference was observed between the doped and undoped poly-Si films. The poly-Si films deposited on quartz exhibited a slight red shift, with peak emission at $\sim$680 nm. Since quartz is transparent at these wavelengths, the emission of these poly-Si films was also measured through the quartz, with no significant difference in the PL spectrum. The PL spectrum from an *n*-type (3.5 Ω cm) *c*-Si(100) substrate, stain-etched for 2 min past t_i indicates almost identical characteristics to that of the poly-Si samples. However, amorphous Si films which were stain-etched did not exhibit a PL signal. It, therefore, appears that for the deposited Si thin films, the level of initial crystallinity plays a greater role than the doping level in obtaining a photoluminescent effect. A more detailed study of the dependence of PL on the crystallinity of the initial poly-Si films will be published elsewhere.

Undoped poly-Si layers on oxidized Si wafers were patterned by electron cyclotron resonance reactive ion etching[7] in Cl_2 at 2 mTorr. The samples were then stain-etched in $HF:HNO_3:H_2O$. Under Hg source UV excitation, PL patterns with good uniformity were obtained over large areas and with high resolution in small features. In Fig. 3, several light-emitting poly-Si patterns are shown. The top pattern consists of 6 μm wide lines on 12 μm centers. The middle pattern combines relatively large PoSi areas (45×70 μm^2) with fine light-emitting lines (0.7 μm). Finally, the bottom pattern consists of five parallel lines rang-

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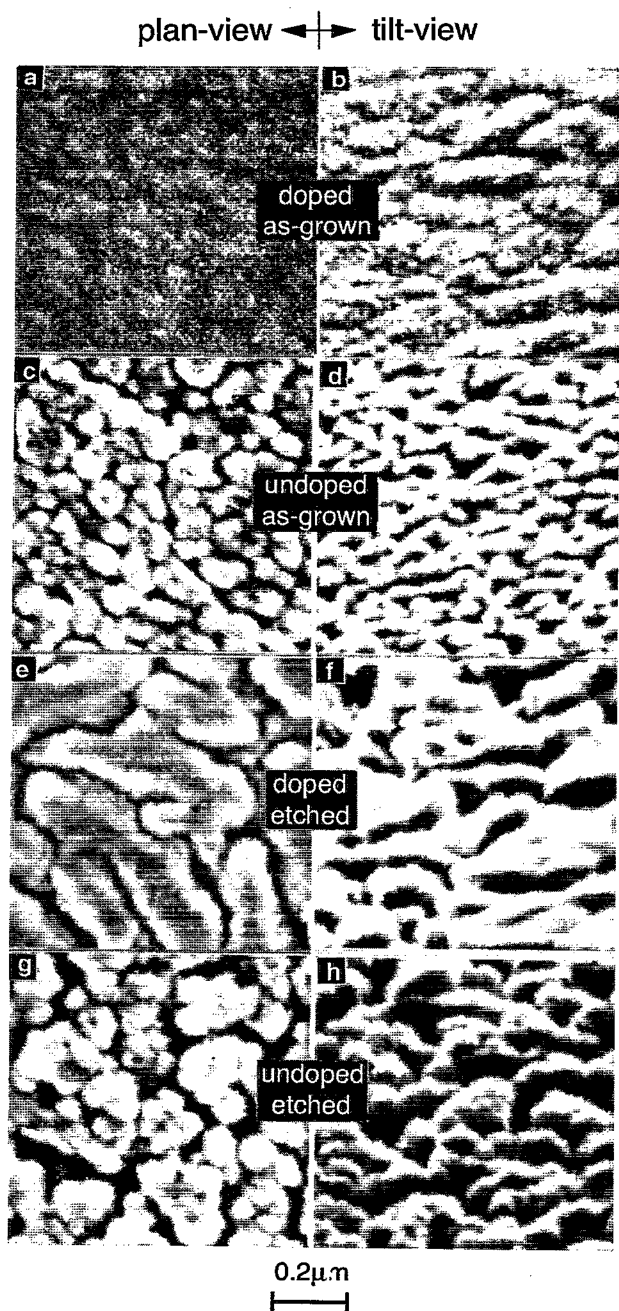

FIG. 1. Surface morphology (SEM) of as-grown [(a)–(d)] and stain-etched [(e)–(h)] doped and undoped poly-Si films.

ing from 0.6 to 1.0 μm in 0.1 μm increments. It is interesting to point out that for these fine lines, the line width is only a factor of 3–5 times larger than the grain size shown in Fig. 1, yet a uniform and continuous photoemissive pattern is obtained.

In summary, room temperature visible photoluminescence was obtained from polycrystalline Si thin films upon stain-etching. PoSi patterns with submicrometer dimensions have been fabricated and have exhibited well-defined luminescence, both as isolated features and in combination

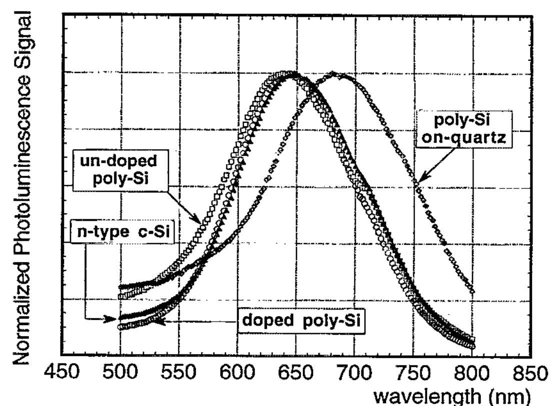

FIG. 2. Photoluminescence spectra: doped and undoped poly-Si o SiO_2/Si stain-etched for 30 s; undoped poly-Si on quartz stain-etched fo 120 s; n-type c-Si stain-etched for t_i plus 120 s.

with much larger areas. The fact that poly-Si films depos ited on oxidized Si wafers and on quartz can be made int efficient light emitters opens up many new applications fo porous Si in integrated optoelectronics, thin film displays etc. Finally, from our experimental results, we conclud that while complete long-range order in the starting mate rial is not necessary for the observation of photolumines cence in PoSi, some level of crystallinity is required.

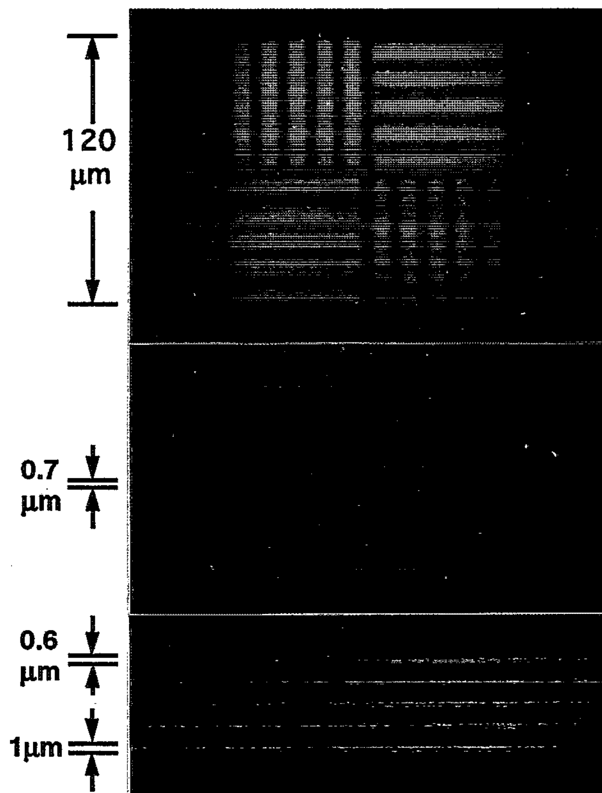

FIG. 3. Light emitting patterns in stain-etched poly-Si on SiO_2/Si.

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