Stain-etched porous silicon visible light emitting diodes

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(Received 18 October 1994; accepted 13 February 1995)

Visible light emitting diodes are fabricated from *p*-type porous silicon (PoSi) thin films (~200 nm) using indium tin oxide (ITO)/PoSi *n-p* heterojunction structures. Uniform PoSi thin layers were produced by pure chemical etching (stain etching) of B-doped single crystalline Si in a $HF:HNO_3$-based solution. Electroluminescence (EL), with a spectrum similar to that of the photoluminescence, was observed from the diodes under forward bias only. The diodes show improved $I-V$ characteristics with an ideality factor of 2.1. An EL onset bias as low as 3 mA/cm^2 was measured.

I. INTRODUCTION

Since the report of visible room temperature photoluminescence (PL) from porous silicon (PoSi),[1] various types of PoSi-based light emitting diodes (LEDs) have been reported by many authors.[2–13] These include Schottky diodes using Au,[2–5] Al,[6] and conducting polymer[7,8] contacts, heterojunctions using indium tin oxide[9,10] (ITO) and silicon carbide,[11,12] and PoSi *p-n* homojunctions.[8,13] In all these examples, the PoSi layer is obtained by anodization in HF-based electrolytes.

While PoSi produced by *purely chemical etching*[14] (stain etching) of crystalline silicon (*c*-Si) or polycrystalline silicon (poly-Si) in $HF:HNO_3$-based solutions exhibits similar PL to that prepared by anodization in HF-based electrolytes, the stain-etching process possesses some unique advantages over anodization in addition to its much greater simplicity. This includes submicron PoSi pattern formation[15] and fabrication of poly-PoSi thin films on glass.[16] The capability of fabricating luminescing PoSi patterns embedded in conventional Si is very important for monolithic integration of optically active Si components onto a Si substrate. In addition, for application in flat panel display devices, the stain-etching technique might well be the only practical method to produce luminescent thin poly-Si films on quartz and glass,[16] because stain etching is performed without the electrode and electrolytic bath required by anodization. However, to date there has been a scarcity of information regarding electroluminescence (EL) in stain-etched PoSi. In this article, we report the fabrication and characterization of ITO/PoSi *n-p* heterojunctions using *stain-etched* PoSi thin films. ITO is a degenerately doped, *n*-type wide-band-gap semiconductor,[17] known to form *n-p* heterojunction diodes[18–20] on conventional *p*-type Si substrates. The high optical transmittance of ITO in the visible range makes it a good candidate as the top electrode for surface emitting EL devices.

II. EXPERIMENT

The process starts with 3 in. *p*-type (100) Si substrates with a resistivity of 6–16 Ω cm. An aluminum film of ~400 nm was sputter deposited onto the backside of the wafer and subsequently annealed in N_2 at 450 °C for 5 min to provide an ohmic contact prior to PoSi formation. A photoresist layer of about 2 μm is spin coated onto the aluminum film and oven baked at 100 °C for 30 min to serve as a protection layer during the stain etching. The front side of the sample was then rendered porous in a solution of $HF:HNO_3:H_2O$ with a 1:3:5 volume ratio for ~1 min beyond the incubation time.[15] An alternative stain-etching process uses a solution of $HF:HNO_3$ with a 200:1 volume ratio for less than 1 min.[21] The stain etching was performed in ambient light at room temperature with no intentional heating. The sample was then rinsed in deionized water and blown dry with nitrogen. An ITO thin film of ~1000 Å was sputter deposited from an ITO target (90% In_2O_3+10% SnO_2) onto the PoSi through a shadow mask. This results in diodes with top transparent circular electrodes of ~0.08 cm^2 area. Alternately, a Au thin layer of ~100 Å is evaporated through the shadow mask onto the PoSi, forming Schottky contacts with same device area. After ITO (or Au) deposition, the backside photoresist was removed by rinsing in acetone. ITO/*p*-Si heterojunctions were also fabricated simultaneously with ITO/*p*-PoSi using the same process except for the stain-etching step. Electrical and optoelectronic measurements were conducted to characterize the device performance. These include current–voltage ($I-V$) characterization and PL and EL measurements. The $I-V$ characteristics were studied using a Hewlett-Packard 4140B pA/DC voltage source. The photoluminescence characterization was described in detail in a previous publication.[21] Electroluminescence spectra are obtained using a 0.25 m monochromator and a photomultiplier detector. In the study of EL intensity versus bias current, the photoemission is coupled into the photomultiplier directly using an optical fiber bundle.

III. RESULTS AND DISCUSSION

The PoSi film obtained by stain etching in this study was very smooth and showed a shiny, mirrorlike dark-blue interference color. The surface morphology and pore sizes were

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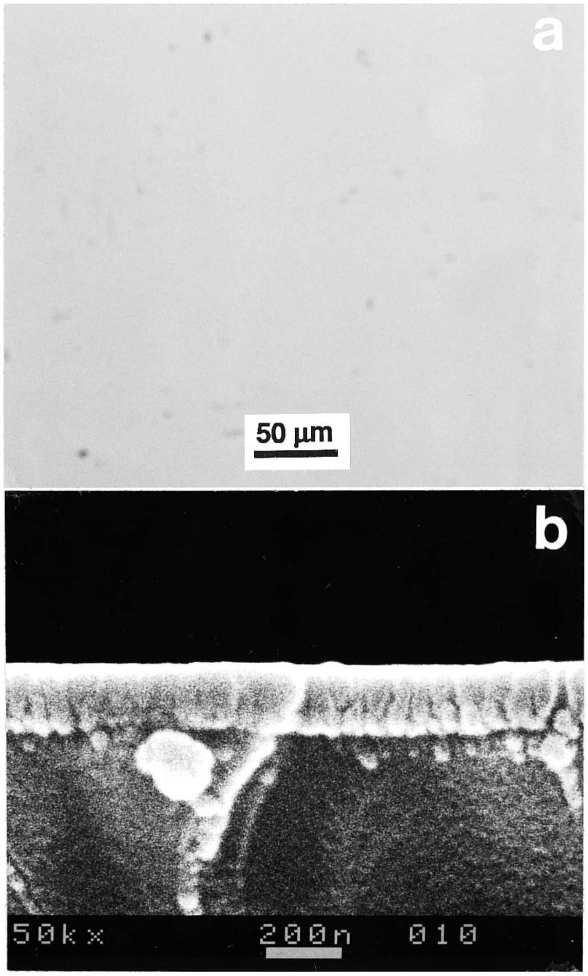

FIG. 1. Photographs of a PoSi thin film obtained by stain etching of B-doped 6–8 Ω cm (100) *c*-Si in $HF:HNO_3:H_2O$ of 1:3:5 composition for 1 min plus 3 min incubation time: (a) plan-view optical microscope image; (b) cross-section SEM image.

studied by optical and scanning electron microscopy (SEM). Figure 1(a) is an optical plan-view microphotograph of a PoSi film etched for a total of 4 min, including a 3 min incubation time. The top surface is clearly observed to be very smooth and uniform. Figure 1(b) is a cross-section SEM microphotograph of the same sample which indicates that the PoSi film has a uniform thickness of about 200 nm. Figure 1(b) also reveals the presence of vertical pores (with diameters of 10–20 nm) existing through the entire thickness of the PoSi layer. No obvious modification of the surface morphology (such as bubbling) was observed during the stain etch. All heterojunctions of ITO to porous Si and to conventional Si exhibited strongly rectifying $I-V$ characteristics. The ITO/*p*-PoSi diode typically turned on at a forward bias (negative voltage on ITO electrode) of less than 1.5 V and had a reverse breakdown voltage in excess of 50 V. Figure 2 shows a typical $I-V$ characteristic of the ITO/*p*-PoSi heterojunction, with the device structure illustrated in the inset. The leakage current density of the diode at a reverse bias of −10 V is ~538 nA/cm^2, which is close to the lowest reported values.[6] The diode has a rectifying ratio of $\sim 1.6\times 10^5$ at ±15 V, which is the highest value reported to date.[7,11] Low-

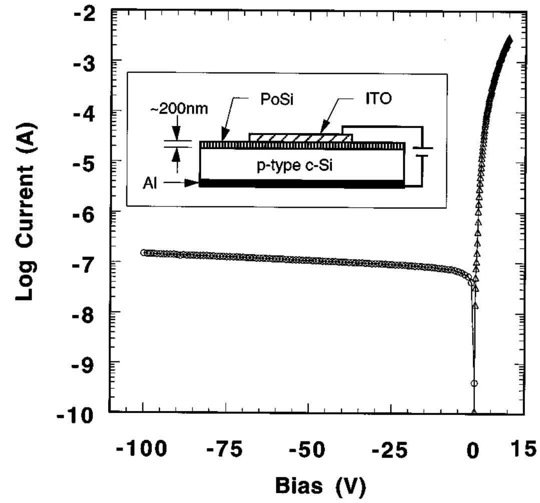

FIG. 2. $I-V$ characteristic of an ITO/*p*-PoSi diode fabricated by stain etching. The inset represents the diode structure under reverse bias.

voltage measurements of the $I-V$ characteristics reveal an ideality factor (n) of ~1.5 for ITO/*p*-Si and ~2.1 for ITO/*p*-PoSi heterojunctions, as shown in Fig. 3. The ideality factor of 2.1 for our *stain-etched* ITO/*p*-PoSi diode is significantly better than the previously reported values of 3.8 for an anodized ITO/*p*-PoSi diode[10] and of 3 for an anodized PoSi p^+-n^+ homojunction.[13] It is also obvious from Fig. 3 that a series resistance exists for both ITO/*p*-Si and ITO/*p*-PoSi diodes. Using the method illustrated in Fig. 3, an r_s of ~135 Ω is calculated for the conventional ITO/*p*-Si diodes (r_s=136 Ω at 1 V and r_s=134 Ω at 0.5 V). However, when the same method is applied to the ITO/*p*-PoSi $I-V$ curve, the r_s obtained is roughly 10–100 times higher than that of ITO/*p*-Si diodes and the series resistance has a strong dependence on the applied bias. The increase in r_s in the PoSi diodes as compared to conventional Si diodes could be a combination of several factors: (a) an effective area which is much smaller than the ITO area because of the columnar nature of the PoSi; (b) the presence of a thicker native oxide layer on the PoSi (Ref. 22) than on conventional Si; (c) carrier depletion[23] in the *p*-PoSi layer. The dependence of r_s on

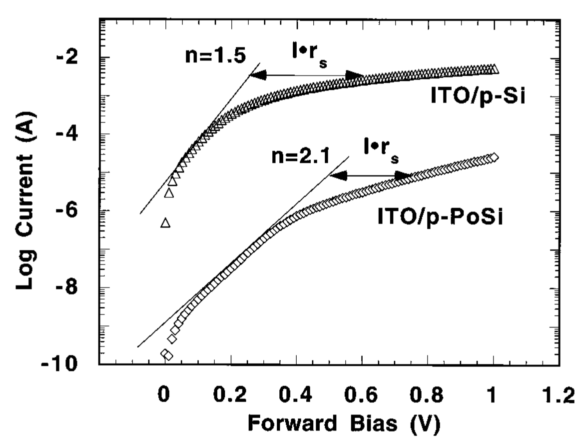

FIG. 3. Low-bias $I-V$ characteristics of ITO/*p*-PoSi and ITO/*p*-Si heterojunctions.

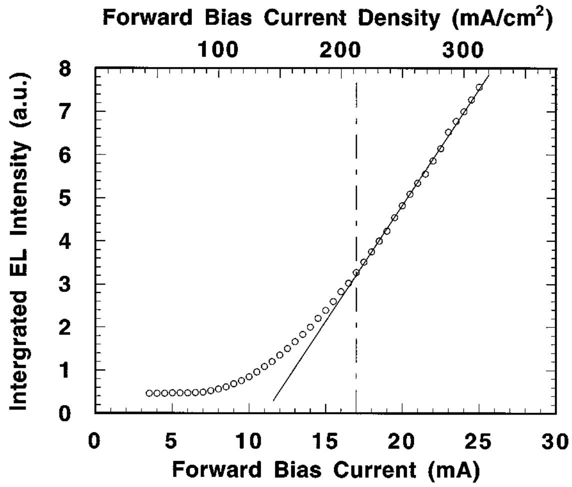

FIG. 4. Dependence of ITO/*p*-PoSi electroluminescence intensity on bias.

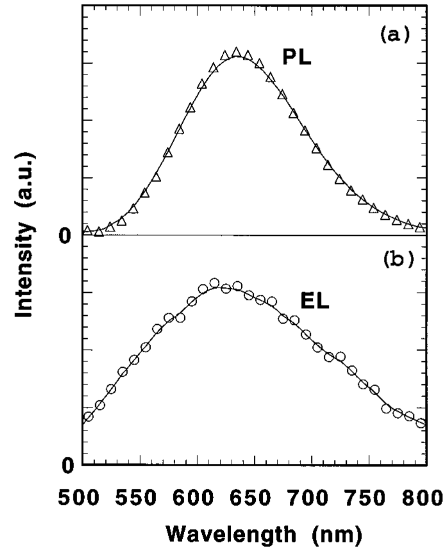

FIG. 6. (a) PL spectrum under 365 nm UV line excitation; (b) EL spectrum at a bias of 125 mA/cm^2.

forward bias voltage could be the result of one or more mechanisms: (a) increased tunneling through the oxide at the ITO/PoSi interface at higher forward bias; (b) reduction in the carrier depletion in the PoSi due to injection. Further study is needed to fully understand the effect of voltage dependence of r_s and to reduce the r_s.

Under forward bias, visible EL was readily observed with the naked eye in a dark background when a current larger than ~10 mA/cm^2 was applied. No EL was observed under reverse bias. Uniform light emission is present over the entire area where the PoSi is in contact with the ITO electrode. No EL is observed from the ITO/*p*-Si heterojunction under similar conditions. The EL color (reddish-orange) is very similar to that of PL under UV (365 nm) excitation. The nondispersed EL intensity increases monotonically with bias as shown in Fig. 4. At low bias, below a current density (J_D) of 213 mA/cm^2, the EL intensity scales with a power law dependence of EL$\sim J_D^m$, where m was calculated to be approximately 2.5. This nonlinear behavior at low bias is similar to that reported by Maruska, Namavar, and Kalkhoran[10] for anodized ITO/*p*-PoSi diodes. The onset current density of 213 mA/cm^2 for linear EL vs J_D dependence obtained here is almost 10 times lower than that of the anodized ITO/PoSi *n*-*p* heterojunction.[10] The EL intensity is stable and reproducible as monitored by a photomultiplier. For example, Fig. 5 plots the EL intensity at a constant current of 10 mA as a continuous function of time for 1 h. It is obvious from Fig. 5 that the EL is quite stable and a variation of only ~6% was observed. The lowest EL onset measured with a photomultiplier was at a bias of ~3 mA/cm^2. To the best of our knowledge, this represents the lowest EL onset reported to date for a non-*p*-*n* homojunction diode structure, and is comparable to the lowest EL onset obtained[24] from a n^+-*p* PoSi diode.

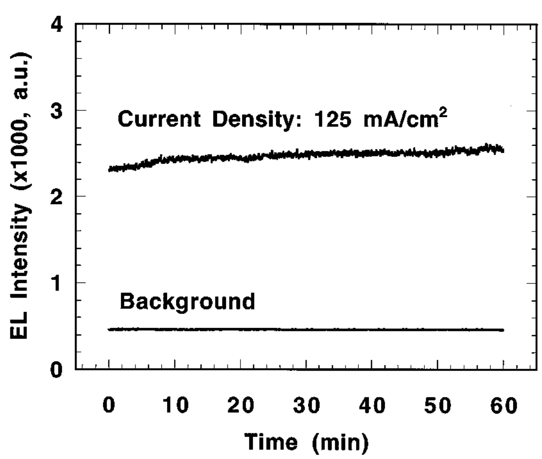

FIG. 5. EL intensity at a current density of 125 mA/cm^2 as a function of time for 60 min.

The PL spectrum, taken from PoSi under UV 365 nm excitation, has a broad emission band, peaked at around ~635 nm as shown in Fig. 6(a). The EL was measured under a forward dc bias at a constant current. Shown in Fig. 6(b) is the EL spectrum from an ITO/*p*-PoSi diode at a current of 10 mA (125 mA/cm^2). The EL has a broad spectrum, similar to that of the PL but with a slightly blue-shifted peak at ~625 nm. While the spectra are not equipment corrected, the similarity in emission spectra suggests that the EL has the same luminescent center as that of the PL.

In comparison with previously published anodized PoSi LED's the characteristics of the stain-etched PoSi LED reported here are significantly improved over the best reported values in aspects such as ideality factor,[10,13] rectifying ratio,[11] EL onset current,[3] and EL linearity.[10] The improvement obtained in PoSi LEDs with stain etching could be attributed to the thinner PoSi films and better uniformity. EL has also been obtained from stain-etched PoSi Schottky diodes using Au thin films (~100 Å).

IV. CONCLUSION

In summary, visible light emitting diodes using stain-etched PoSi thin films have been fabricated and characterized. The PoSi film used in this work of only about 200 nm is the thinnest ever reported for a PoSi LED. The devices have superior electrical characteristics and achieved the best ideality factor, the highest rectifying ratio, and among the lowest EL onset current reported to date along with improved EL linearity. Since the stain-etch process is much simpler than anodization and can be used to form submicron luminescent PoSi patterns and to produce luminescing poly-PoSi films on quartz and glass, these results demonstrate a very promising and advantageous technique for fabrication of PoSi-based LED's and poly-PoSi-based electroluminescent devices.

ACKNOWLEDGMENTS

This work was supported in part by the BMDO/IST and monitored by ARO, under Grant No. DAAL03-92-0290. The authors are pleased to acknowledge the encouragement of L. Lome, M. Littlejohn, R. Trew, and J. Zavada.

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