Visible Electroluminescence from Stain-Etched Porous Si Diodes

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***Abstract*— Visible electroluminescence (EL) from stain-etched porous silicon (PoSi) films is presented. The PoSi thin layers (∼200 nm) were obtained by stain-etching of *B*-doped 6–16 Ω-cm (100) crystalline Si in a HF:HNO_3: H_2O (1 : 3 : 5) solution. Indium tin oxide (ITO) films of ∼2500 Å were used to form a Schottky contact. Visible EL was observed at room temperature from the diode under forward bias. EL onset bias as low as 3 mA/cm^2 was measured. The EL, with an emission peak at ∼640 nm, is similar to the photoluminescence under UV excitation, indicating the same luminescent centers. This result demonstrates a promising and simple technique for the fabrication of PoSi-based light emitting diodes and flat panel display devices.**

I. Introduction

THE REPORT of strong visible photoluminescence (PL) at room temperature obtained from porous silicon [1] (PoSi) has triggered great interest in achieving Si-based optoelectronic devices in spite of the lack of complete understanding [2] of this phenomenon. A few authors have reported visible electroluminescence (EL) from solid-state Schottky contacts between a PoSi layer obtained from *anodically* etched crystalline Si (c-Si) and thin films of Au [3]–[6], Al [7], indium tin oxide (ITO) [8], [9], or conducting polymer [10], [11]. EL was also reported from an anodized PoSi *p-n* homojunction [12] and a SiC/PoSi heterojunction [13], [14]. The available device characteristics of anodized PoSi light emitting diodes (LED's) reported to date are summarized in Table I. The table indicates the device's structure, the thickness of the PoSi layer, the leakage current density at a given reverse bias voltage, the current rectification ratio obtained between given forward and reverse bias voltages, the current density (bias) required for onset of EL (both visually observable and photodetector measured), and the peak wavelength of the EL spectrum.

Photoluminescent PoSi can also be easily obtained by *purely chemical etching* (stain-etching) [15] of c-Si or poly crystalline Si in HF:HNO_3-based solutions. While the underlying mechanism of PoSi formation is the same for both techniques, the stain-etching process is much simpler and is, therefore, easier to be integrated into existing Si technology. More importantly, only stain-etching has the demonstrated capability [16] to achieve sub-micron luminescing PoSi patterns embedded in conventional Si. This capability is very important for monolithic integration of optically active Si components onto a Si substrate. In addition, for application in flat panel display devices, stain-etching has the advantage to easily produce photoluminescent poly-PoSi films on quartz and glass [17], without the need of an electrode as required in anodization. However, to date there has been a scarcity of information regarding EL in stain-etched PoSi. In this letter we report visible EL from stain-etched thin PoSi films, with a spectrum very similar to that of the PL.

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TABLE I
SUMMARY OF PoSi LED CHARACTERISTICS

Device Structure	PoSi Layer (μm)	Leakage		Rectification		EL Onset (mA/cm^2)		EL Peak Wavelength (nm)	Ref. No.
		Current (nA/cm^2)	Reverse Bias (V)	Ratio	Voltage (V)	Photo-detector	Visually Observable		
Au/PoSi	7.5	-	-	-	-	-	14	650	3
Au/PoSi	5.5	-	-	-	-	11	133	480, 540, 650	4
Au/PoSi	1-10	-	-	-	-	600	10^4 (V/cm)	650	5
Au/PoSi	3-7	2×10^5	7	420	±7	> 50	90	680	6
Al/PoSi	-	177	10	-	-	-	30	-	7
ITO/PoSi	-	-	-	-	-	-	-	650	8 & 9
Polymer/PoSi	4	2×10^5	10	1000	±15	30	-	593	10
Polymer/PoSi	7	-	-	-	-	-	5	630	11
p-PoSi/n-PoSi	-	-	-	-	-	-	600	640	12
SiC/PoSi	-	4×10^3	1	2.5×10^4	± 1	-	2×10^4	670	13
SiC/PoSi	-	10^4	5	100	± 5	-	12	700	14
ITO/PoSi	0.2	538	10	1.6×10^5	±15	3	10	640	This work

II. Experimental

The starting material was *B*-doped CZ (100) Si substrates (6–16 Ω-cm). An aluminum film was sputtered onto the back side of the wafer and subsequently annealed to provide an ohmic contact prior to PoSi formation. The front side of the sample was then rendered porous by stain etching in a mixture of HF:HNO_3:H_2O (1:3:5 volume) for 1 min beyond the incubation time [16]. At the same time Al was protected by photoresist. Stain-etching was performed in ambient light at room temperature. Immediately after stain-etching, the sample was rinsed in deionized water and blown dry with nitrogen. An indium tin oxide (ITO : 90% In_2O_3 + 10% SnO_2) thin film of ∼2500 Å was deposited onto the PoSi samples through a shadow mask resulting in transparent circular electrodes with an area of either ∼0.08 cm^2 or ∼0.26 cm^2.

III. Results and Discussion

The PoSi film obtained was very smooth, as revealed by optical and scanning electron microscopy (SEM), and showed a shiny, mirror-like dark-blue interference color. No obvious modification of the surface morphology (such as bubbling) was observed during the stain-etch. Cross-section SEM analysis of the samples indicates that the PoSi film has a uniform thickness of about 200 nm, with the presence of vertical pores (with diameters of 10–20 nm) existing through the entire thickness of the PoSi layer. The device structure is illustrated in the inset of Fig. 1, implementing a Schottky diode between the ITO and the PoSi film. The diode exhibited strongly rectifying I-V characteristics as shown in Fig. 1. The diode turned on at a forward bias of around 1.5 V and had a reverse breakdown voltage in excess of 50 V. Typical leakage current density of the diodes at a reverse bias of -10 V was $\sim$538 nA/cm^2, which is close to the lowest reported value [7]. The diodes have a rectifying ratio of 1.6×10^5 at ± 15 V, which is the highest value reported to date (see Table I). Visible EL was readily observed with the naked eye in a dark background when a forward current larger than 10 mA/cm^2 was applied. No EL was produced under reverse bias. The observed EL color (reddish-orange) is very similar to that of PL under UV (365 nm) excitation. The EL intensity, measured with a DR-1 A Digital Radiometer from Gamma Scientific, increases monotonically with current. The EL intensity is stable and reproducible. An example is contained in Fig. 2, where EL intensity is shown as a function of diode current. The two sets of data displayed are taken from the same diode, with two hours of electrical aging under continuous dc current of 10 mA (40 mA/cm^2) between the two sets of measurements. During the aging period, the emission was continuously monitored at a current of 10 mA and a variation of less than 5% was observed. From Fig. 2, the EL intensity increases with a power law dependence on the current (EL $\sim J_D^m$), with a power of 2 to 3. This behavior is similar to that reported by Maruska *et al.* for anodized ITO/PoSi diodes [18]. However, further work is needed to understand this nonlinear dependence, especially at low bias where $m \sim 3$ was observed. The lowest EL onset observed with a photodetector was obtained at $\sim$3 mA/cm^2. The inset in Fig. 3 is an EL image from a diode under a forward current density of $\sim$40 mA/cm^2. It can be seen that uniform light emission is produced from the area where the PoSi is in contact with the ITO electrode, in other words where electron injection occurs under forward bias. No EL is observed when the ITO is deposited directly on c-Si.

PL and EL spectra were recorded using a 0.5 m monochromator with a photomultiplier. The PL was excited with a filtered UV 365 nm line from a 100 W Hg lamp. EL was measured at a forward dc bias of 190 mA/cm^2. Shown in Fig. 3 are examples of typical PL and EL spectra. The PL, taken from PoSi through the 95% transparent electrode, has the familiar spectrum of stain-etched PoSi [16] peaked at around 650 nm with a full width at half-maximum (FWHM) of $\sim$100 nm. The EL has a spectrum very similar to that of the PL with a peak at 640 nm. The similarity in emission spectra strongly suggests that the EL from the PoSi layer is caused by the same luminescent center as that of the PL. This is in strong contradiction to the only previous report of EL from chemically etched Si [19]. In that case, the EL and PL peak positions are separated by more than 190 nm and it was suggested that a different mechanism was responsible for the EL [19].

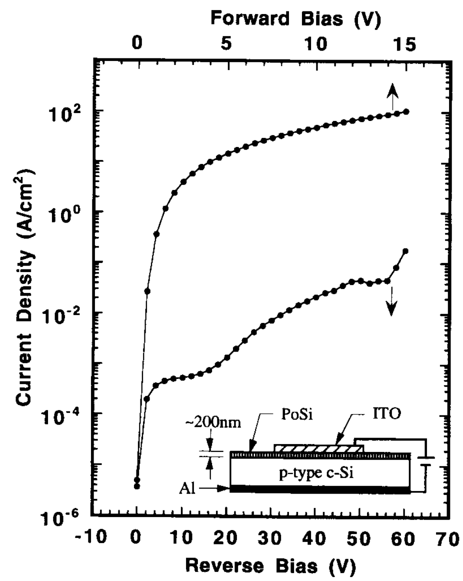

Fig. 1. I-V characteristic of an ITO/PoSi diode fabricated by stain-etching. The inset represents the diode structure.

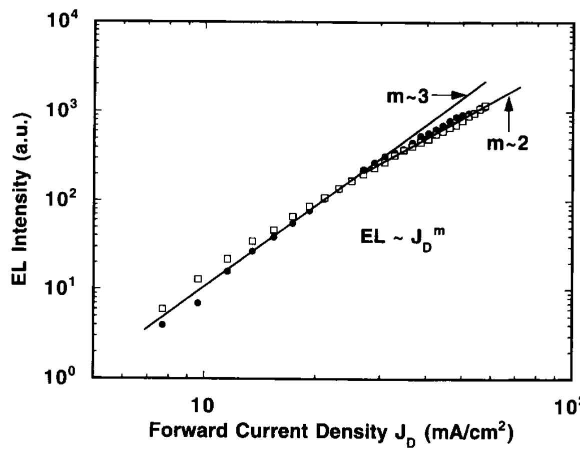

Fig. 2. Dependence of stain-etched porous-silicon LED electroluminescence intensity on device current density. The filled circles represent data from the first measurement and the open squares represent data from the second measurement after two hours electrical aging of the device under 40 mA/cm^2 bias.

The characteristics of the stain-etched PoSi LED reported here are compared in Table I with previously published anodized PoSi LED's. It is clear from the comparison that by employing a thin and uniform stain-etched PoSi layer, the device characteristics were significantly improved in areas such as leakage current, rectifying ratio, and EL onset current. However, the intensity and efficiency of EL from stain-etched (and anodized PoSi) still need to be significantly improved in order for device applications to become practical. EL has also been obtained from stain-etched PoSi Schottky diodes using Au thin films ($\sim$100 Å). The results are similar to those of the ITO/PoSi diodes described above.

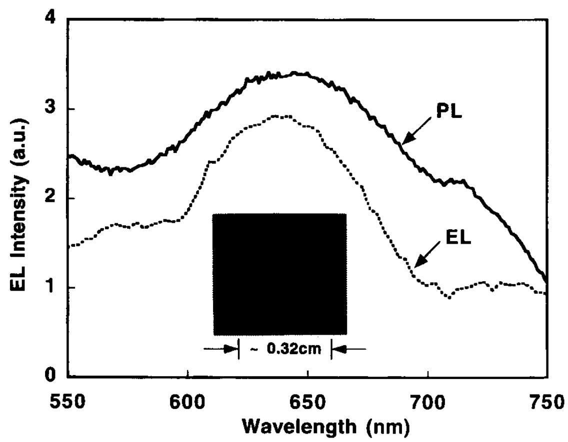

Fig. 3. PL and EL spectra from an ITO/PoSi diode under 365 nm UV line excitation and a forward bias of 190 mA/cm^2, respectively. Inset shows a black and white version of an original color (reddish-orange) EL image from an ITO/PoSi diode (with area of $\sim$0.08 cm^2) under a forward bias of 40 mA/cm^2. The dark spike protruding into the light region is the shadow of the probe tip used for applying bias to the ITO electrode.

IV. Conclusion

In summary, EL has been obtained from stain-etched PoSi thin film diodes using ITO and Au Schottky contacts. The PoSi film used in this work of only about 200 nm is the thinnest ever reported for a PoSi LED. The device has superior electrical characteristics and achieved the lowest EL onset current. Since the stain-etch process is much simpler than anodization and can be used to form sub-micron 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 flat panel displays.

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