Electroluminescence in silicon oxynitride films

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We report electroluminescence (EL) from 50 nm silicon oxynitride films on *p*-type crystalline silicon substrates in a Au/silicon oxynitride/Si structure. The EL intensity has a peak below 2.45 eV, and is consistent with radiative recombination of injected carriers. The EL is present only in annealed samples, and the emission is similar to the photoluminescence from the same samples. The current–voltage behavior is indicative of space charge-limited current. No polarity or field dependence of the EL peak energy is observed. This phenomenon is attributed to the relaxation of carriers down the band tails before recombination. © *1999 American Institute of Physics.*
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INTRODUCTION

Recently, many attempts to obtain efficient electroluminescence (EL) from a silicon-based device have been made, as the applications of such a device in optoelectronics are numerous. Such attempts include devices incorporating nanoclusters of silicon in a silicon dioxide matrix,[1,2] and porous silicon.[3] Recently, EL has been reported for silicon oxide,[4–6] nitride,[7,8] and oxynitride[9] thin films in which electrons and holes are injected from opposite sides of the film and radiatively recombine. We have previously reported intense photoluminescence (PL) in amorphous silicon oxynitride films,[10–12] and now report EL in these films in a Au electrode/silicon oxynitride/crystalline silicon structure.

EXPERIMENT

Samples were fabricated using 1.25 in. diameter, 0.009–0.011 in. thick, (100) *p*-type Si wafers with 2 Ω cm resistivity which were RCA cleaned and quartered. A thermal SiO_2 film was grown on the entire substrate and then etched away in the center of the quarter wafers with concentrated HF. The remaining oxide prevents leakage current around the edges of devices that are subsequently fabricated on the substrate.

Immediately after the etch procedure the substrates were placed under vacuum in the deposition chamber. Silicon oxynitride films were grown for 9 min by radio frequency plasma-enhanced chemical vapor deposition using 20 sccm 5% SiH_4 in He and 13 sccm 10% N_2O in He as the reagent gases. The deposition conditions were: power, 35 W; pressure, 0.1 Torr; and substrate temperature, 300 °C. After deposition, some films were annealed at 950 °C in a quartz tube furnace for 30 min in 100 sccm flowing 10% H_2 in N_2. The thickness and index of refraction (n) of the films were measured using single-wavelength ellipsometry at 633 nm. The thickness of the samples was 53 ± 3 nm, and samples were grown with $n=1.66\pm0.01$ because we have previously shown that such samples exhibit strong PL.[10–12] Additional fabrication and composition details are published elsewhere.[10,11] For the top contact a gold film less than 15 nm thick and with an area of approximately 0.5 cm^2 was evaporated onto the silicon oxynitride at a base pressure of 5×10^{-8} Torr. Back contacts were made with Ga/In eutectic. The device structure is shown in Fig. 1.

Measurements of the PL and EL spectra were made with a single-grating spectrometer and a GaAs photomultiplier tube (PMT). The PL excitation source was a 325 nm HeCd laser. EL and current-versus-voltage ($I-V$) measurements were made using a 60 V/250 mA dc power supply. The absolute sensitivity of the PMT was calibrated using a 1 mW HeNe laser. EL efficiency was measured by placing the sample directly in front of the PMT and acquiring intensity versus voltage data. The spectral response for both the grating/PMT system and the PMT alone were measured. While EL efficiency measurements are corrected for the spectral response of the PMT, a straightforward correction of the PL and EL spectra results in misleading artifacts. Thus spectra will be shown as-measured and the effect of spectral response will be indicated.

RESULTS AND DISCUSSION

The PL from a device without a top electrode, shown in Fig. 2, consists of a single peak at 2.85 eV, similar to the 325 nm excited PL we reported previously.[10] Both the dip in intensity around 2.8 eV and the sharp dropoff in intensity at energies below 2.4 eV in the PL (and EL) spectra are artifacts of the spectral response of the system. Note that the division of the 325 nm excited PL intensity into a double peak reported in Ref. 10, although measured with a different optical system, is also due to the spectral response of the system. After deposition of a 10 nm gold film for the top contact, the PL intensity is reduced by approximately an order of magnitude due to reflection of the exciting beam and absorption of the emitted light by the gold film, but the shape of the peak is not affected.

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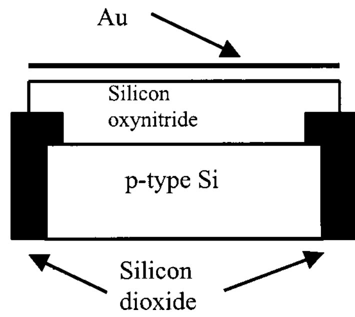

FIG. 1. Structure of electroluminescent device.

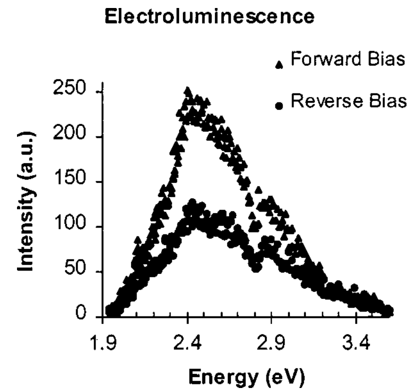

FIG. 3. EL emission intensity vs energy for EL device under both forward and reverse current of 145 mA.

Upon application of a voltage above threshold, the samples exhibited electroluminescence that appears blue to the eye. The turn-on voltage for forward bias (Au electrode negative and the Si substrate in accumulation) was from 2 to 4 V depending on the sample, and for reverse bias was 4–6 V. EL spectra for a constant current of 145 mA are shown in Fig. 3 for 8 V forward bias and 30 V reverse bias on the same sample. The EL under both polarities appears to have a single peak below 2.45 eV, but because of the relative insensitivity of the optical system at low energies the precise peak position cannot be determined. Samples that received no anneal did not exhibit EL.

$I-V$ curves for a typical sample under forward and reverse bias conditions are shown in Fig. 4. In all of the samples measured, the relationship between the forward current I and the bias voltage V can be described as $I-V^b$ where b is between 1 and 2.3 and varies from sample to sample. Such a relationship is indicative of space charge-limited current, with larger exponent b indicating an increase in the number of trap states in the film bulk and/or more balanced electron and hole currents.[13] The reverse current exhibits a power-law dependence on applied voltage, but with a magnitude lower than the forward bias current.

We have shown[10] the absorption edge of our silicon oxynitride films to be greater than 5 eV, so we may approximate the device as a metal-insulator-semiconductor (MIS) structure with the forward-bias band structure shown in Fig. 5. At high enough voltages, electrons and holes can tunnel through the barriers at the silicon oxynitride interfaces into the bulk of the film. In a MIS diode, two factors determine the $I-V$ characteristic: bulk conduction in the insulator, and carrier injection at the insulator interfaces. If one or the other of these effects is dominant, then the $I-V$ curve will be characteristic of that conduction or injection mechanism. Thus, the space charge-limited current characteristic under forward bias indicates that current in this case is limited mainly by bulk conduction. Under reverse bias, the $I-V$ characteristic is also indicative of bulk-limited conduction, but the lower magnitude of the reverse current suggests injection of carriers at the interface (probably by Fowler–Nordheim tunneling[14]) is also limiting the current. No common trends in the variation of EL intensity with current were discernable from sample to sample, but under both forward and reverse bias the EL intensity increased supralinearly with current. The magnitude of the maximum power efficiency (defined as optical power out/electrical power in) for the brightest sample has a lower limit of 4×10^{-6} in forward bias and 7×10^{-7} in reverse bias. The actual values are higher than this since the absorption of the top gold film was not taken into account. The EL efficiency increases monotonically with increased voltage until device burnout. A similar effect is observed in some *a*-Si *p-i-n* diodes and attributed to the increased carrier concentration at higher injection levels.[15] The radiative recombination probability of an electron-hole (e-h) pair decreases exponentially with increasing spatial separation of the pair levels.[15] Because a higher current density leads to a decreased average carrier separation, the average recombination probability of each e-h pair

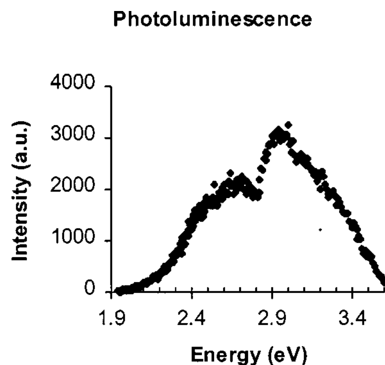

FIG. 2. PL emission intensity vs energy for EL device.

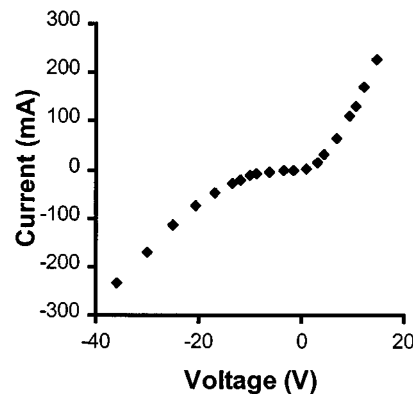

FIG. 4. Current vs applied voltage for EL device.

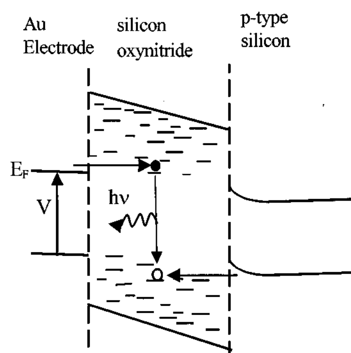

FIG. 5. Energy band diagram for electroluminescent MIS device under forward bias voltage V. The electron (●) tunnels into the silicon oxynitride layer from the Au electrode and recombines with the hole (○) which tunneled from the silicon substrate.

can increase with increased current density. This simple picture should be applied with caution, however, as it ignores contributions from nonradiative recombination, and we have no direct evidence (such as shorter recombination lifetimes) that the increased carrier concentration is the reason for increasing EL efficiency at higher currents.

We believe the EL results from recombination of electrons and holes, but are not able to determine whether both carrier types are injected or whether the recombination takes place between injected majority carriers and trapped minority carriers. Theoretically that information is contained in the exponent b of the $I-V$ curve, and/or the variation of EL intensity with current.[13,16] A detailed study of identical samples of varying thicknesses would be helpful in extracting this information, but at present we have too much sample-to-sample variation in the precise electronic properties of the devices to attempt such a study.

Similar to what was reported by Boonkosum *et al.*,[8] we observe a redshift in the EL peak energy compared to the PL peak energy. We have shown that the PL in these materials is geminate recombination and that the PL peak energy is as much as 1 eV lower than the excitation energy.[10] The latter effect is because the excited carriers very quickly relax in energy down the band tails before recombination. In contrast to PL, EL arising from carrier injection is necessarily a nongeminate process. As the carriers travel through the material before recombination, they will energetically relax down the band tails. The EL peak energy is thus dependent on the amount of relaxation by the carriers before recombination. We have shown that the recombination lifetime in the case of PL is less than 10 ns, and that significant carrier relaxation occurs on this time scale. In the case of EL, if an injected electron and hole must travel for more than 10 ns before encountering one another, it is probable that they will have relaxed to near the end of the tail states before recombination and therefore the EL peak energy will be considerably redshifted from the case of the PL. In addition, this EL peak energy will not depend strongly on recombination lifetime for times much longer than 10 ns, since after this time carriers will already have relaxed to near the bottom of the tail states. We therefore expect no dependence of the EL peak on either the polarity or an increase in the applied field unless this increase lowers the recombination lifetime below 10 ns.

Since we in fact observe no dependence of EL peak energy on polarity or applied field, we suggest that the recombination lifetime is indeed longer than 10 ns. In order to examine whether this is a reasonable number in silicon oxynitride, we calculated that, assuming the entire applied voltage is across the silicon oxynitride layer, the average effective carrier mobility must be less than 5×10^{-4} cm^2/V s. By comparison, the electron mobility in a-SiO_2 is 20 cm^2/V s and the hole mobility is 4×10^{-9} cm^2/V s at room temperature.[17] The authors were not able to obtain a published value for mobility in a-Si_3N_4. However, in Si_3N_4, hole conduction dominates.[18] In addition, the carrier trapping probability is five orders of magnitude higher in silicon nitride than in silicon dioxide, and the average distance carriers travel in Si_3N_4 before being trapped or scattered is only about 35 Å,[19] and the space-charge limited current in our films indicates a significant amount of trapping. Thus an average carrier mobility of less than 5×10^{-4} cm^2/V s is reasonable for our silicon oxynitride films and carrier relaxation explains the redshifted, field-independent EL peak.

In our previous reports,[10–12] we discussed in detail the PL behavior of silicon oxynitride films having similar composition to those in this work. We showed that annealing the films at 950 °C increases the PL intensity by two orders of magnitude, and characterized both the as-deposited and annealed films. We proposed that the PL results from geminate recombination of electron-hole pairs at localized, nonparamagnetic recombination centers. We have suggested the centers are related to Si–Si or Si–H bonds and that the effect of the 950 °C anneal is to increase the number of these centers, and that EL is observed only in annealed samples suggests that the recombination centers for EL and PL are the same.

Another report of EL in MIS diodes incorporating silicon oxynitride is the study by Li *et al.*[9] on ultrathin (~8 nm) silicon oxynitride layers. They report no PL, and EL only under forward bias. In addition, the samples in the Li study achieved maximum intensity after a 600 °C anneal, with high temperature anneals being less effective. Our attempts to observe EL in devices with oxynitride layers significantly less than 50 nm were not successful, but we did not study layers as thin as those in the Li study. Thus it appears that the injection mechanisms and/or the recombination centers are different for our films. Finally, while the efficiency of our films is currently quite low, considerable improvement can be expected through optimization of the device fabrication procedure.

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