Red electroluminescence in Si^{+}-implanted sol–gel-derived SiO_2 films

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We report on a continuously emitting electroluminescent device fabricated by Si^{+}-ion implantation and subsequent annealing of a SiO_2 layer on a silicon substrate. The SiO_2 layer with a thickness of 250 nm was prepared by the sol–gel technique. Four different Si^{+}-ion energies and implantation doses were applied in order to obtain a flat Si^{+}-ion profile across the SiO_2 film thickness with an atomic Si excess of 5%. Electroluminescence (EL) occurs above a low-voltage threshold ($\sim$5 V, 1 A/cm^2) at one bias polarity only even if the device in fact does not exhibit rectifying properties. EL microscopy reveals that EL at 295 K is emitted from a small number of bright spots with diffraction-limited size. EL spectra of individual bright spots were measured using an imaging spectrometer. The wide EL emission band (situated in the red region $\sim$750 nm) obtained with spatial averaging over the semitransparent indium–tin–oxide contact represents the envelope of these individual contributions. We suggest that the EL is due to electron–hole injection into Si nanocrystals which create several conductive percolation paths across the SiO_2 film. Shunting current paths due to defects exist in parallel and are probably the main factor responsible for low EL efficiency (10^{-5}%). [S0003-6951(00)01545-X]

The current interest in light-emitting silicon nanocrystals (Si-nc) is motivated mainly by the need to reconciliate microelectronics (based on Si) with optoelectronics (active elements based on III–V semiconductor). One of the promising techniques being used to elaborate on Si-nc is the implantation of Si ions into SiO_2 films, followed by high-temperature annealing.[1] While most of such films are fabricated by thermal oxidation of crystalline-Si wafers,[2–4] an alternative approach is the deposition of SiO_2 on various substrates by the sol–gel technique. These sol–gel-derived SiO_2 films have proven, e.g., to be excellent matrices for CdS nanocrystals.[5,6]

Recently we have shown, however, that the photoluminescence (PL) of sol–gel-derived Si^{+}-implanted SiO_2 films situated in the blue spectral region is probably due to postimplantation defects and not due to Si-nc.[7] Such samples do not emit any electroluminescence (EL). In this letter, we wish to show that an improved implantation procedure (which introduces a constant profile of Si^{+}-ion density across the thickness of the implanted film) can lead to the appearance of a red PL band [typical of Si-nc (Refs. 8–10)]. Moreover, such samples can exhibit also red EL emission that, we believe, originates in percolating Si-nc.

The samples were prepared in the following way: A sol–gel SiO_2 film was prepared from a mixture of tetramethoxysilane (TMOS), methanol (MeOH), acidic water (HNO_3), and formamide (CH_4NO) in the ratios TMOS:MeOH:H_2O:formamide=1:9:5:1. One hour after mixing the reactants, the solution was deposited by spin coating at 3000 rpm on an *n*-type [100] crystalline-Si substrate. Then, the samples were annealed in air at 500 °C for 1 h. The thickness of such sol–gel films was estimated to be 0.25 ± 0.05 μm. Implantation with Si^{+} ions was done with four different energies and ion doses (20 keV/5.5×10^{15} cm^{-2}, 30 keV/4.5×10^{15} cm^{-2}, 40 keV/1×10^{16} cm^{-2}, and 70 keV/3×10^{16} cm^{-2}) in order to obtain a flat ion profile across the SiO_2 film thickness, with peak excess atomic Si concentration of 5%. Postimplantation annealing was performed at 1100 °C in vacuum for 1 h. Finally, on the top of the implanted films, indium–tin–oxide (ITO) transparent contacts with diameters of 2 mm were evaporated [Fig. 3(d)]. The

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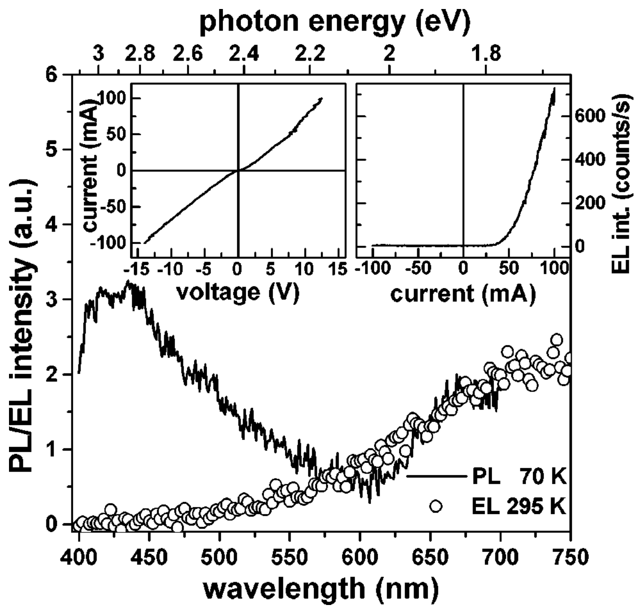

FIG. 1. Comparison of PL (full line) and EL (symbols) spectra. Left inset demonstrates the almost linear electric behavior (I–V curve) of the device. The film conductivity is $\sim 5\times10^{-6}$ $(\Omega\,\mathrm{cm})^{-1}$. Right inset: current dependence of the spectrally integrated EL intensity. Corresponding current densities range from 0 to 3.2 A/cm^2. An onset voltage of approximately 5 V (30 mA) for the light emission can be deduced from the plot.

occurrence of Si-nc was evidenced by Raman analysis that was performed in a reference sample (prepared in exactly the same way but on a quartz substrate instead of the *c*-Si substrate). The Raman spectrum contains a distinct peak around 490 cm^{-1} due to Si–Si vibration in Si-nc.[1]

EL was excited via a continuous dc voltage applied across the implanted SiO_2 film between the ITO contact and the *c*-Si substrate. As an excitation source for PL measurements, either a cw Xe lamp (370 nm) or 3 ns pulses of the third harmonics (354 nm) from a Nd:YAG laser were used. All experiments were performed at room temperature, except the PL measurements in Fig. 1, where the sample was cooled down to 70 K in order to enhance the signal level.

The PL and EL emission spectra are displayed in Fig. 1. It can be seen that the PL contains both a blue (defect-related) band at ~440 nm and a red (Si-nc-related) emission band at ~750 nm. The EL intensity as a function of the injection current is depicted in the right inset in Fig. 1. There are two quite remarkable features: First, the blue part of the spectrum is completely cut in EL and only the red band is present. Second, the EL is emitted in one polarity of the applied voltage only (positive on the *c*-Si substrate). We call this polarity ''forward bias,'' even if the sample has in fact no electric rectifying properties (see the left inset in Fig. 1).

We interpret these observations as a manifestation of Si-nc in the implanted SiO_2 film. These nanocrystals create percolation conductive channels through the SiO_2 film which are statistically distributed over the ITO contact. The electric current flowing through these transport channels injects electrons and holes into the Si-nc and subsequent radiative recombination gives rise to EL emission. It is interesting to note that in formerly studied samples[11] with a thicker (540 nm) oxide layer implanted with only one acceleration voltage for the Si ions, the Si-ion distribution has a Gaussian profile and is well separated from the surface and the substrate. In order to obtain EL in such a situation, a voltage applied across the sample must reach several hundreds of V and the EL shows a blue component only. In this case, light emission is not due to carrier percolation between Si-nc but to hot electrons in the active part of the implanted layer.

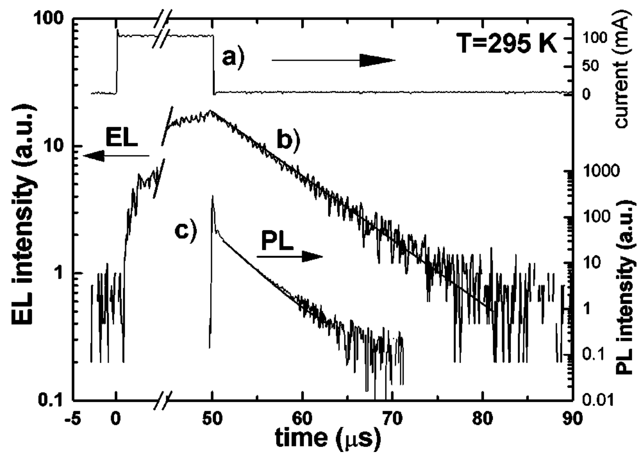

FIG. 2. Time-resolved PL and EL measurements. Upper trace (a) represents a 50 μs injection current pulse with ''forward'' bias of 14 V. Lower traces correspond to EL (b) and PL (c) decays and both of them are approximated by single exponentials (straight lines) with the decay times $\tau_{\mathrm{EL}}=8$ μs and $\tau_{\mathrm{PL}}=2.5$ μs.

To check the above conjecture about percolating Si-nc, we have performed experiments with time- and spatially resolved EL measurements. The results of the time-resolved EL study are shown in Fig. 2. Upper curve (a) represents an injection current pulse of 50 μs duration. Its rectangular shape means that the current rise time is very short and cannot be resolved on the time scale tens of μs. Curve (b) in Fig. 2 shows the relevant EL response (integrated spectrally and also spatially over the whole ITO contact), with clearly expressed EL rise and decay. The EL decay can be fitted as a single exponential with the time constant $\tau_{\mathrm{EL}}=8\pm1$ μs. Curve (c) in Fig. 2 represents the temporal profile of the red PL band (detected at 680 nm) in the same sample under excitation with a 354 nm pulses of 3 ns duration. Apart from a very short spike at the beginning, the PL decay can again by approximated by an exponential decay with $\tau_{\mathrm{PL}}=2.5$ μs. This good agreement between PL and EL dynamics, along with the identical spectral position of the red bands (Fig. 1), indicate clearly that this red light emission has the same origin.

We note that the above spectroscopic data imply that this origin must reside in Si-nc because both the spectral position and the decay time (on a microsecond scale) are characteristic of exciton radiative recombination in Si-nc.[9,10] The blue PL emission band appearing frequently in sol–gel-implanted derived SiO_2 films is much faster (on the time scale on nanoseconds[7]). In fact, we could have introduced a model giving rise to a stretched exponential decay as one usually does for Si-nc and porous Si.[9] As Fig. 2(c) indicates, this becomes relevant at longer time delays but for the purposes of this letter we did not attempt to do this.

Spatially resolved EL studies are demonstrated in Fig. 3. An optical microscope image of the ITO contact of the sample is shown in Fig. 3(a) (taken in reflection of an external illumination, without applied bias). The same contact as

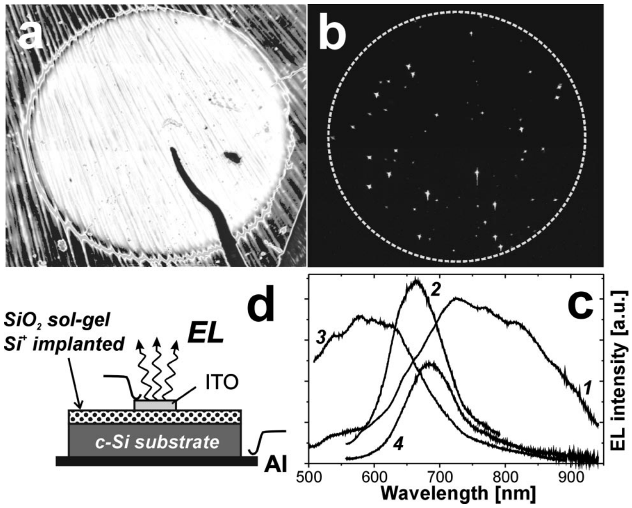

FIG. 3. (a) Microscope view of the illuminated ITO contact without applied bias. The dark line at the bottom is a contact pad. The diameter of the contact is 2 mm. (b) EL emitted from the same contact under forward bias of 10 V/60 mA. The EL radiation occurs in discrete bright spots. (c) EL spectra of several single bright spots. (d) Schematic drawing of the device.

observed in darkness via the microscope under applied ''forward'' bias of 10 V is displayed in Fig. 3(b). EL radiation can be clearly seen, which occurs in bright spots dispersed over the surface of the contact. Figure 3(c) shows examples of individual emission EL spectra of several of such single spots (for the experimental setup see Ref. 12). All these spectra are situated at the red end of the visible region.

The data in Fig. 3 again strongly support the interpretation outlined above. The bright spots represent points where the percolation threshold (low-resistance path) for the electric current has been reached to flow across the implanted SiO_2 film. This part of the current flowing through interconnected Si-nc ''chains'' is due to injection of carriers into the Si-nc. The blue emission (see PL, Fig. 1) cannot be excited electrically because defects responsible for this radiative channel obviously do not represent a good transport path either for electrons or for holes. There is still a possibility to excite the centers responsible for the blue emission by impact ionization of the hot electrons. However, because the percolation effect reduces the resistance of the implanted film, sufficiently high electric field cannot be achieved.[13] The red PL/EL band in Fig. 1 represents, therefore, an inhomogeneously broadened envelope of individual emission bands [Fig. 3(c)], which originate in different current paths through the Si-nc.

We have to note that spatially resolved PL reveals also site-dependent variations, mainly, varying relative intensity of blue and red emission bands. This fact points to the existence of an inhomogeneous distribution of Si-nc and defects in the sol–gel layer. It is, however, difficult to find a correlation between EL and PL variations as the excitation mechanism and tested depth are quite different.

One important observation remains to be explained still, namely, the occurrence of EL in one polarity of the applied bias only. This can be understood easily using a simple model involving the carrier transport through the (n-type substrates Si-nc separated by SiO_2 barriers/ITO contact) system. We recall that ITO is a degenerate wide-gap semiconductor of n type containing virtually no free holes. Under ''forward'' bias (positive potential on the substrate) both electrons from ITO and holes from the substrate are injected into the film and tunnel through SiO_2 into Si-nc quantized levels. Their radiative recombination gives rise to EL. This EL is relatively weak (the external quantum efficiency averaged over the contact is about $\sim 10^{-5}\%$), because the holes are minority carriers in the substrate. Under ''reverse'' bias only electrons from the substrate can be injected into the Si-nc, no e–h recombination is possible and no EL is observed, even if the current of the same order of magnitude as in ''forward'' still flows. This model also explains the observation of a voltage (current) threshold for EL, as shown in the right inset in Fig. 1: Increasing ''forward'' bias lowers bandbending at the Si-nc/SiO_2 interface. Narrowing of the barriers facilitates carrier tunneling through SiO_2. Thus, a definite minimum bandbending (voltage) is needed for holes to tunnel through SiO_2 into Si-nc and to assure a continuous hole injection. An obvious hint how to increase the EL efficiency of our device is then to use a Si substrate of p type instead of n type. This should lead to a substantial increase in the efficiency of electron–hole pair injection.

In conclusion, we have implanted Si ions into a sol–gel-derived SiO_2 film in such a way that we obtained a flat excess Si-ion profile (5 at. % of Si) across the film thickness. While PL contains both a defect-related blue emission band and a Si-nc-related red one, in EL only the red band survives. We have observed that EL occurs in discrete spots only and we succeeded in measuring emission spectra of single spots. We have several strong experimental indications that this EL radiation originates in Si-nc that create percolation conducting paths through the SiO_2 matrix, even if we cannot provide any direct evidence for it. The flat profile enables us to obtain EL at low voltages.

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[1] T. Shimizu-Iwayama, M. Ohshima, T. Niimi, S. Nakao, K. Saitoh, T. Fujita, and N. Itoh, J. Phys.: Condens. Matter **5**, L375 (1993).
[2] H. Z. Song and X. M. Bao, Phys. Rev. B **55**, 6988 (1997).
[3] L. Rebohle, J. von Borany, R. A. Yankov, W. Skorupa, I. E. Tyschenko, H. Fröb, and K. Leo, Appl. Phys. Lett. **71**, 2809 (1997).
[4] M. L. Brongersmaa, P. G. Kik, A. Polman, K. S. Min, and H. A. Atwater, Appl. Phys. Lett. **76**, 351 (2000).
[5] J. Butty, N. Peyghambarian, Y. H. Kao, and J. D. Mackenzie, Appl. Phys. Lett. **69**, 3224 (1996).
[6] A. Othmani, J. C. Plenet, E. Bernstein, C. Bovier, J. Dumas, P. Ribblet, P. Gilliot, R. Levy, and J. B. Grun, J. Cryst. Growth **144**, 141 (1994).
[7] J. Dian, J. Valenta, K. Luterova, I. Pelant, M. Nikl, D. Muller, J. J. Grob, J.-L. Rehspringer, and B. Hönerlage, Mater. Sci. Eng., B **69-70**, 564 (2000).
[8] S. Guha, J. Appl. Phys. **84**, 5210 (1998).
[9] J. Linnros, N. Lalic, A. Galeckas, and V. Grivickas, J. Appl. Phys. **86**, 6128 (1999).
[10] J. Valenta, J. Dian, K. Luterova, P. Knapek, I. Pelant, M. Nikl, D. Muller, J. J. Grob, J.-L. Rehspringer, and B. Honerlage, Eur. Phys. J. D **8**, 395 (2000).
[11] D. Muller, P. Knapek, J. Faure, B. Prevot, J. J. Grob, B. Hönerlage, and I. Pelant, Nucl. Instrum. Methods Phys. Res. B **148**, 997 (1999).
[12] J. Valenta, N. Lalic, and J. Linnros, Opt. Mater. (in press).
[13] J.-Y. Zhang, Y.-H. Ye, and X.-L. Tan, Appl. Phys. Lett. **74**, 2459 (1999).