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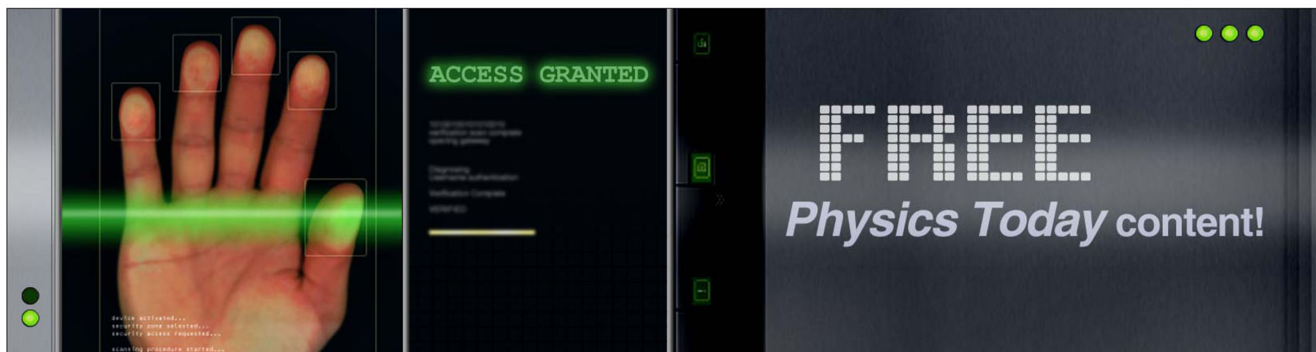

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Visible photoluminescence from pressure annealed intrinsic Czochralski-grown silicon

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Visible luminescence from thermal treated intrinsic Czochralski-grown silicon is reported. Oxygen precipitates were formed in a nearly oversaturated silicon by a two-step thermal treatment with auxiliary use of high pressures. A wide photoluminescence band peaked at about 2.3 eV is observed in those samples for which the first treatment was performed at a relatively high temperature and which show a higher amount of oxygen precipitates and oxygen related defects. Scanning electron microscopy of the best performing samples show the presence of submicron conglomerates on the surface. We have tentatively attributed the luminescence emission to the defects in the suboxide SiO_x phase formed in the oxygen precipitates. © *1996 American Institute of Physics.* [S0003-6951(96)03345-1]

The search for efficient emission from silicon is one of the main tasks to develop a low cost silicon based photonics technology. Several alternative approaches have been followed in the past to reach such a goal.[1] The most successful attempt to date is the use of partial anodical electrochemical dissolution of Si wafers to yield porous silicon, a material which luminesces with about 10% efficiency at room temperature and in the visible.[2] Driven by these results, various techniques to obtain Si nanostructures have been proposed where quantum confinement of the photoexcited carriers and efficient nanocrystal surface passivation are both present.[3] An interesting approach has been the implantation of Si ions into silica films followed by thermal treatments which produces Si nanocrystals with room-temperature visible emission.[4] A weak visible photoluminescence has also been observed in Si from the damaged regions full of nanocavities created by heavy H or He bombardment and successive thermal annealing.[5,6] Following all these works, in this research we propose a new technique to obtain luminescence from silicon, based on the isolation of nanometric suboxide SiO_x particles in oxygen precipitates, in order to mimic the local structures found in oxygen passivated Si nanocrystals.

Czochralski-grown (CZ) silicon contains high amounts (10^{17}–10^{18} cm^{-3}) of interstitial oxygen. Different techniques have been developed to stimulate the oxygen precipitation in silicon.[7] Recently, a new approach has been proposed to thermal annealing of CZ silicon with the auxiliary use of high hydrostatic pressures.[8] A typical treatment consists in preannealing of CZ silicon under ambient pressure in N_2 atmosphere at temperatures up to 1000 K, in order to create small oxygen clusters which serve as nucleation centers for precipitation. In a successive annealing step at 1270–1420 K for up to 200 h, oxygen precipitates and oxygen-related defects are formed. The samples are then subjected to additional thermal treatment at high (typically 1 GPa) hydrostatic pressures in argon atmosphere. Depending on details of the processing, such as temperature, time and pressure, clusters, and precipitates of oxygen are formed with dimensions varying from a few angstroms to a few tenths of a micron.[8] A Fourier transform infrared spectroscopy study has shown that up to 80% of the interstitial O present in as-grown CZ silicon can be trapped into these precipitates.[9] Different commercially available CZ-silicon crystals with the same initial oxygen concentration give similar results.[8]

All samples in the present study have been obtained from a single (001) oriented p-type CZ-silicon wafer of 0.6 mm thickness. Before annealing the hole concentration was at 1×10^{15} cm^{-3} level and the oxygen contents close to oversaturation (1.1×10^{18} cm^{-3}). The thermal treatments which have been used for various samples are reported in Table I. These samples are representative of others which have been annealed at 750, 950, and 1400 K for periods varying from 5 to 20 h. Some of these were additionally treated at 1200–1450 K at a pressure of 10^9 Pa. The last treatment induces oxygen precipitates as well as other oxygen-related defects, like stacking faults, saucer pits defects, and prismatic dislocation loops defects. Densities of these defects can be evaluated in transmission electron microscopy and, after selective surface etching, in polarized-light microscopy or scanning electron microscopy. As an example, sample 1, which gives naked-eye visible photoluminescence at 80 K and whose thermal story is given in the table, contains stacking faults and dislocations at 1.8×10^6 and 0.7×10^6 cm^{-2} concentrations, respectively, and almost no other defects like saucer pits or prismatic defects.

TABLE I. Thermal history of the various samples. The second–fourth columns refer to the temperature and duration of the various thermal treatments. The last column refers to the percentage of the oxygen initially present in the wafer and which forms the precipitates. It was measured by Fourier transform infrared absorption spectroscopy in Refs. 8 and 9.

Sample no.	First annealing	Second annealing	Third annealing and pressure treatment	Oxygen precipitate (%)
1	750 K/20 h	950 K/20 h	1200 K/1 GPa/5 h	85
2	1100 K/20 h	1350 K/10 h	⋯	45
3	750 K/20 h	1350 K/20 h	⋯	45
4	750 K/20 h	950 K/20 h	⋯	10

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(Yang etch[7] has been used). In addition, more than 80% of the initial oxygen concentration has precipitated in this sample. It turns out, that changing slightly the time and/or temperature of the third, pressure annealing, different types of defects can dominate, maintaining constant their overall concentration.

Scanning electron microscopy images of samples 1–3 are shown in Fig. 1. These samples were not subjected to chemical etching, to avoid any modification of light-emitting, near-to-surface layers. In the pressure-treated sample (No. 1) irregular-shaped, submicron ''bubbles'' with high secondary emission coefficient are visible [Fig. 1(a)]. These are tentatively assigned to SiO_x aggregates. Similar to, but of smaller dimensions, electron re-emitting dots are also visible in sample 2 [Fig. 1(b)]. Numerous other samples examined by SEM do not reveal any inhomogeneity on the surface. However, prolonged exposure of some of them (e.g., sample No. 3) to a high-energy (30 keV) electron beam opens spherical-like cavities [see Fig. 1(c)]. Reference sample No. 4 gives a homogeneous SEM picture.

Photoluminescence (PL) was excited by using the 488 nm line of an argon-ion laser with a maximum power density of 17 W/cm^2 or the third harmonic at 355 nm of a Nd:YAG (yttrium–aluminum garnet) laser. A SPEX double spectrometer followed by an RCA 31034A02 photomultiplier interfaced to a standard photon counting system was used to record the spectra. The samples were placed in a liquid-nitrogen flux cryostat to change the temperature.

Photoluminescence was observed for samples No. 1–3 but not for the reference sample 4. At 80 K bright yellowish photoluminescence from sample 1 is also easily visible by the dark-adapted naked eye. PL spectra of samples 1–3 are shown in Fig. 2. A wide emission band covering more than 300 meV, peaked at about 2.3 eV and with a long low energy tail is observed in the three samples. Some differences in intensity and spectral position among them are observable. Sample 1 shows the most intense emission which is slightly redshifted with respect to the other samples. The intensity of PL in this sample depends on the position on the surface of the spot [compare the two curves in Fig. 2(a)]. A time degradation of the luminescence intensity which lowers to 1/2 of the initial emission in the first 30 min but remains stable afterwards has also been observed. Sample 2 exhibits a lower overall emission intensity than sample 1. However, no temporal degradation or surface inhomogeneity in its emission properties have been observed. Its spectral line shape is independent on the excitation energy [see Fig. 1(b) full line and dots]. Please note that the additional, low energy peak observed for the 355 nm excitation is probably due to an experimental artifact. Due to a different focalization of argon and Nd:YAG laser beams we cannot judge absolute PL intensities comparing signals in Fig. 1(b). However, comparative studies performed using a 1000 W xenon lamp and covering the 500–380 nm range indicate little dependence of PL intensity on the excitation wavelength.

Detailed studies of PL spectra in the 80–300 K range also show a rather weak dependence of the emission on the temperature for moderately cooled samples. The PL signal falls off by merely 30% when the temperature raises from 80 to 250 K. Then it drops by a factor of three raising further temperature to 300 K. However, it is still measurable at room temperature. No changes as a function of the temperature are observed in the spectral line shape and position.

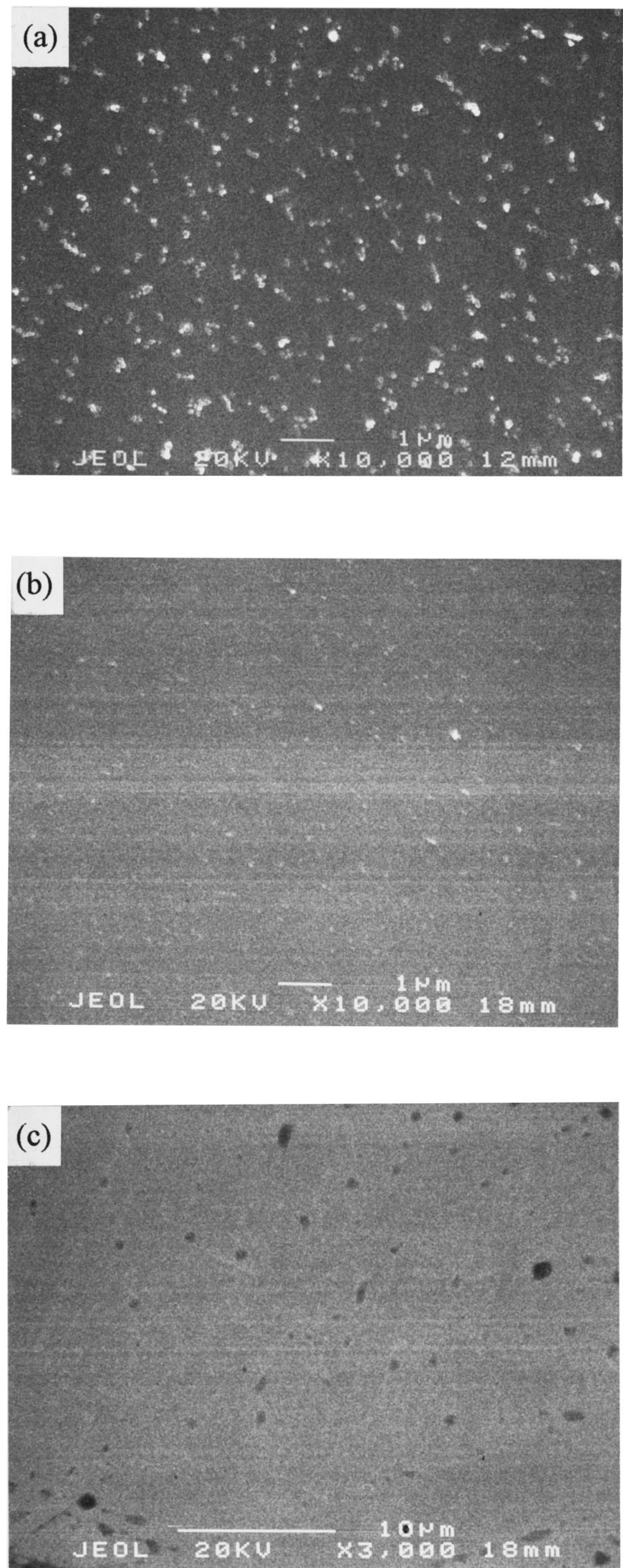

FIG. 1. Scanning electron microscopy (secondary emission signal) photographs of thermal and/or pressure treated CZ-Si samples. JEOL 3000 instrument used. (a) sample 1; (b) sample 2; (c) sample 3 after *in situ* electrobeam etching. See Table I for sample description. Note a different magnification factor for insets (a), (b), and (c).

Comparing our different samples we conclude that PL

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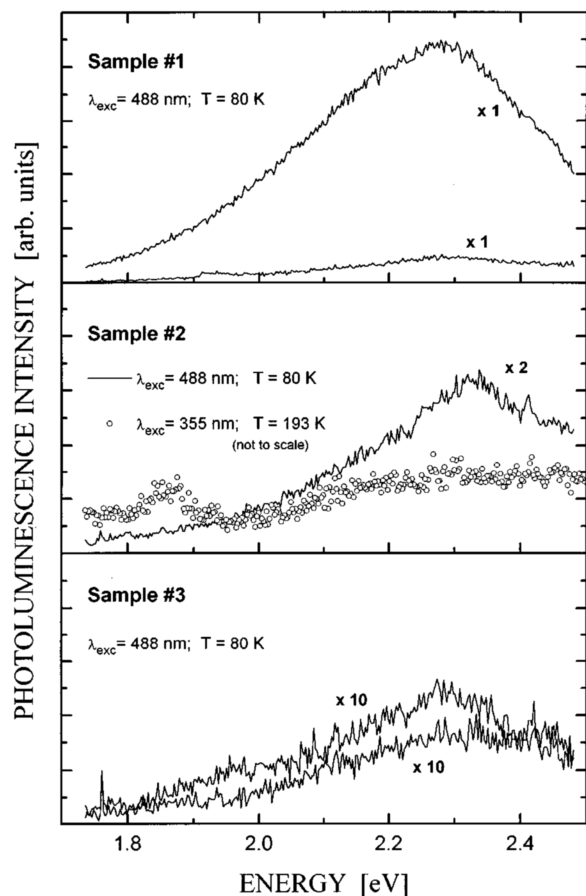

FIG. 2. Photoluminescence spectra of three samples. The top panel refers to sample 1 and reports two spectra taken on two different points on the sample surface. The middle panel refers to sample 2 and reports two spectra excited by two different wavelengths and temperatures. The bottom panel refers to sample 3 and reports two spectra taken on two different points on the sample surface. λ_{exc} is the excitation wavelength. The relative sensitivity factors have been given for the spectra taken at 80 K and with $\lambda_{exc}=488$ nm. The spectrum excited with $\lambda_{exc}=355$ nm is not directly comparable because of a different excitation intensity used and sample absorption coefficient at this wavelength.

can be obtained either in an intermediate/high temperature (1000/1350 K) two step slow (20 h/10h) annealing or in a low-temperature (750/950 K) preannealing combined with the final, intermediate temperature (1200 K) pressure treatment. In both cases, the overall concentration of oxygen related defects after treatment is of 3×10^{6} cm^{-2} order but different kinds of defects dominate for each sample. Annealing at high pressures, leading to an almost complete precipitation of the interstitial oxygen, is allowed to form centers with a very high PL brightness.

In the following, we consider two possible models for the luminescence: (i) the emission originates from defects formed in small SiO_x particles due to the O precipitation;[7] and (ii) the luminescence is due to nanometric Si regions surviving among the O precipitates.[5,6] Some signature of the presence of SiO_x particles can be inferred from the SEM images in which higher secondary emission indicates a nonconducting phase. We are well aware that it is very difficult to give a sound interpretation of our data on the basis of only the luminescence measurements, hence work is in progress to characterize a morphological and structural point of view of these samples. However, a lot of work has already been performed in the literature about the green band observed in Si nanocrystals (see Ref. 4 and references cited therein) and the so-named blue emission in porous silicon (see Ref. 10 and references cited therein). Following the analysis and the discussions reported in these works we are lead to the conclusion that the luminescence we observed could be described by model (i). In fact model (ii) which relies on excitons confinement in nanocrystals should rather be disregarded due to the insensitivity of PL line shape and spectral position on the sample treatment, on the density of precipitates and on the excitation wavelength. To the contrary, model (i) which relies on the emission from defects in the suboxide phase formed in the precipitates is compatible with our experimental observations.

In conclusion, visible luminescence in thermal annealed intrinsic CZ silicon has been observed. A tentative attribution of the emission to defects formed in the suboxide SiO_x particles due to the oxygen precipitation induced by thermal treatments has been proposed. Positron annihilation studies[11] to relate the absolute PL intensity to the size and concentration of different defects induced by oxygen precipitation are under way.

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[1] S. S. Iyer and Y.-H. Xie, Science **260**, 40 (1993).
[2] L. T. Canham, Appl. Phys. Lett. **47**, 1046 (1990).
[3] L. Brus, R. W. Collins, M. Hirose, and F. Koch, Mater. Res. Soc. Symp. Proc. **358**, 157 (1995).
[4] G. Ghislotti, B. Nielsen, P. Asoka-Kumar, K. G. Lynn, A. Gambhir, L. F. Di Mauro, and C. E. Bottani, J. Appl. Phys. **79**, 8660 (1996).
[5] L. Pavesi, G. Giebel, R. Tonini, F. Corni, C. Nobili, and G. Ottaviani, Appl. Phys. Lett. **65**, 454 (1994).
[6] D. Bisero, F. Corni, C. Nobili, R. Tonini, G. Ottaviani, C. Mazzoleni, and L. Pavesi, Appl. Phys. Lett. **67**, 3447 (1995).
[7] A. Borghesi, B. Pivac, A. Sassella, and A. Stella, J. Appl. Phys. **77**, 4169 (1995).
[8] A. Misiuk, B. Surma, and J. Hartwig, Mater. Sci. Eng. B **36**, 30 (1996).
[9] A. Misiuk, Proc. SPIE **2373**, 335 (1995).
[10] L. Tsybeskov, Ju. V. Vandyshev, and P. M. Fauchet, Phys. Rev. B **49**, 7821 (1994).
[11] R. S. Brusa, M. Duarte Naia, A. Zecca, C. Nobili, G. Ottaviani, R. Tonini, and A. Dupasquier, Phys. Rev. B **49**, 7271 (1994).

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