Photoluminescence from nanocrystalline silicon nc-Si, nc-Si/SiO2 nanocomposites, and nc-Si oxidized in O2 and treated in H2O

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Photoluminescence from nanocrystalline silicon nc-Si, nc-Si/SiO$_2$ nanocomposites, and nc-Si oxidized in O$_2$ and treated in H$_2$O

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I. INTRODUCTION

In their article, Weeks *et al.* reported on photoluminescence (PL) from nanocrystalline silicon (nc-Si) oxidized at low temperature in oxygen and water with maximum intensity at about 1.65 eV (~750 nm).[1] When about 4 nm sized Si nanocrystals were exposed to water vapor at about 100 °C for 8 h, the PL appeared with the highest intensity. For the purpose of the following discussion, the authors reproduce this PL curve from Fig. 4 of Ref. 1 in present Fig. 1 (see red asterisks; note that the apparent spectral distribution of the curves in Fig. 1 may be influenced by the spectral sensitivity of the different detectors and cut-off filters used in the given works, as mentioned, e.g., in Ref. 2 and shown also in Fig. 1 of Ref. 3).

Weeks *et al.* quote several publications on PL from nc-Si and correctly state that the origin of the PL in different publications is not always clear. In fact, there have been a number of publications on PL from nc-Si, from porous Si (P-Si), and from hydrogenated silicon clusters where the origin of the PL, as well as the post-treatment of the sample after their preparation, has not been unambiguously documented. In some cases, the PL appeared only after several days of the exposure of the samples to air. In this short note, we shall only show that the PL from nc-Si/SiO$_2$ nanocomposites and that from silanols ≡Si–O–H have different spectral distribution and also different characteristics. Whereas the PL from nc-Si/SiO$_2$ nanocomposites has a maximum intensity at about 1.5–1.6 eV (around 800 nm), the PL from the silanol appears as a broad feature with a maximum around 2.8–3 eV (see Fig. 1). The PL from alanols ≡Al–O–H shows a similar behavior. We further briefly summarize the optoelectronic properties of nc-Si imbedded in a SiO$_2$ matrix including the question of possible size dependence of the energy and intensity of the PL emission.

II. PHOTOLUMINESCENCE FROM nc-Si/nc-Si/SiO$_2$ NANOCOMPOSITES AND FROM SILANOLS AND ALANOLS

The PL from nc-Si/SiO$_2$ nanocomposites—where silicon nanocrystals of a size chosen between about 2 and 10 nm are imbedded in SiO$_2$ matrix, shown in Fig. 1 as black dots—has been obtained from thin films of nc-Si prepared either by chemical transport in hydrogen plasma or by plasma chemical vapor deposition from silane diluted with hydrogen at deposition temperature chosen between about 70 and 300 °C, and controlled substrate bias (see Fig. 1 in Ref. 4 and Figs. 1 and 2 in Ref. 5). The deposited nc-Si films have been controllably oxidized in 99.998% pure oxygen at 870–1200 °C for different times, followed by post-treatment in forming gas at about 350–450 °C.[2,3] Treatment in forming gas (4–10 vol. % H$_2$ in ultrapure N$_2$) is a standard procedure used in the semiconductor industry to reduce defects, e.g., in the gate oxide (e.g., Ref. 6). The oxidation of the as deposited nc-Si occurs within the grain boundaries uniformly through the whole thickness of the films. By an appropriate choice of the deposition temperature, substrate bias, and oxidation
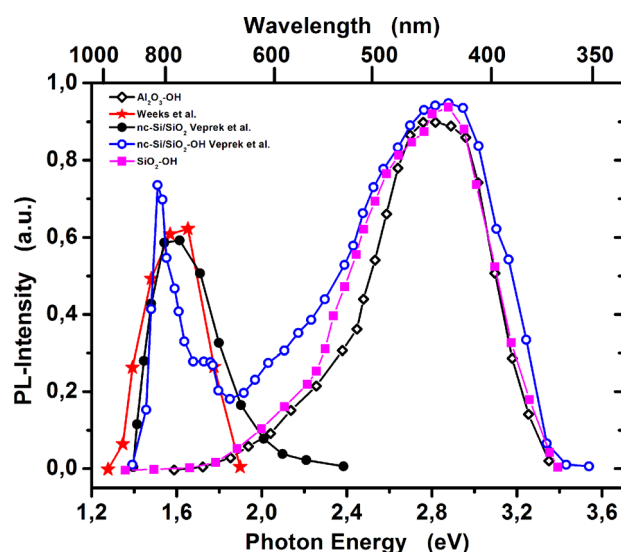

FIG. 1. (Color online) Photoluminescence from 4 nm size silicon nanocrystals oxidized in water vapor at 100 °C (red asterisk, see Fig. 4 in Ref. 1), from nc-Si/SiO$_2$ nanocomposites treated in forming gas (black dots, see Fig. 1 in Ref. 2 and text for details), nc-Si/SiO$_2$ nanocomposites exposed to boiling ultrapure water and treated in forming gas (blue open circles, see Fig. 2 in Ref. 8), finely dispersed SiO$_2$ treated in water and forming gas (see full magenta squares, Fig. 2 in Ref. 8) and Al$_2$O$_3$ treated in boiling water and forming gas (open black diamonds, see Fig. 2 in Ref. 8).

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temperature and oxidation time, we were able to prepare nc-Si/SiO$_2$ nanocomposites with crystallite size controlled between about 2 and 10 nm, and a well-defined separation between the Si nanocrystals in the SiO$_2$ matrix. The latter is important because only when the separation is sufficiently large, i.e., $\geq$1 nm, the PL intensity is high. For example, for a crystallite size of about 2–2.5 nm, the PL intensity decreased by 2 orders of magnitude when the average distance between the Si nanocrystals decreased from >1 nm to few tenths of nanometers, because the wave-functions in different nanocrystals overlap and the quantum confinement was lost (see Fig. 2 in Ref. 7). For a given crystallite size and large separation between the Si nanocrystals, the PL intensity has been optimized by controlled oxidation and annealing in forming gas (see, e.g., Fig. 1 in Ref. 2). We refer to our earlier papers for further details of the controlled preparation and processing of the nc-Si/SiO$_2$ nanocomposites.[2,3,5,7,8]

The spectral distribution of the PL from the nc-Si/SiO$_2$ nanocomposites and the position of the maximum intensity, shown in Fig. 1 as black dots, remained essentially unchanged regardless of the crystallite size varying from about 10–2 nm (see Fig. 4 in Ref. 9), where the large increase of the bandgap of the nc-Si occurs (see Fig. 4 in Ref. 5). This increase of the bandgap (see Fig. 2) is seen in PL from porous Si (e.g., Ref. 10), Si nanowires (e.g., Refs. 11–13) passivated by chemisorbed, i.e., covalently bonded hydrogen, or from nc-Si passivated by organyls (e.g., by allylbenzene[14]) covalently bonded to nc-Si. Also, the PL decay time $\tau_{1/2}$ of about 10^{-5}–10^{-4} s at the photon energy of about 2 and 1.4 eV, respectively (see Fig. 8 in Ref. 15), did not change with the crystallite size in that range [Fig. 4(b) in Ref. 15]. Finally, this PL did not show any polarization memory, which suggested that the absorbing and radiating centers are different entities (see Fig. 7 in Ref. 15).
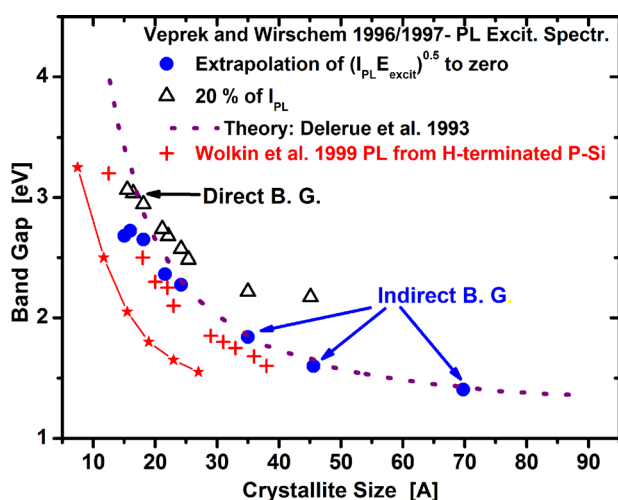

FIG. 2. (Color online) Dependence of the band gap on the crystallite size of nc-Si evaluated as indirect (blue full symbols) and direct (open triangles) bandgap (Ref. 29), from porous Si passivated with chemisorbed hydrogen (Ref. 10) (red crosses), from Si nanowires passivated with chemisorbed hydrogen (Ref. 12) (red asterisk), and theoretical calculations by Delerue et al. (Ref. 30) (dotted line).

However, the intensity of this PL increases with decreasing size of the nc-Si as expected from the quantum confinement model (e.g., Ref. 16) and shown in Fig. 2 of Ref. 2, and in more detail in Fig. 6 of Ref. 5. Therefore, this PL has been attributed to a combined process involving the photon adsorption in nc-Si [which follows the quantum confinement dependence regarding the increasing transition probability with decreasing crystallite size (see Fig. 4(a) in Ref. 15 and Fig. 6(a) in Ref. 5) and bandgap as shown in Fig. 2] followed by fast energy transfer to the nonbinding oxygen hole centers (NBOHC) in the SiO$_2$ matrix from which the PL occurs. This mechanism has been confirmed by the measurements of the corresponding electron spin resonance signal, which scales with the PL intensity (see Figs. 4 and 5 in Ref. 17), and further substantiated by theoretical density-functional based tight-binding molecular-dynamics and semiempirical molecular orbital calculations.[18] Therefore, there is little doubt that the "red" PL with peak intensity around 1.6 eV (black full symbols in Fig. 1) is from NBOHC and not from silanol groups. We suggest that also the PL reported by Weeks et al. (red asterisk in Fig. 1) is of similar origin, may be from different defect sites, but not from silanol groups, because of a different spectral distribution of PL from silanols, as will be shown now.

We became interested in the PL from silanol groups because, in the course of our studies in early 1990s, when one coworker has found that upon a storage of the nc-Si and nc-Si/SiO$_2$ samples in laboratory air, a green–blue PL appeared whose intensity increased with the time of the storage (see Fig. 2 in Ref. 19 and the discussion therein). Such PL has been observed also by several other groups, and it has often been attributed to quantum confinement in nc-Si. We shall not discuss this issue further here.

To avoid artifacts due to poorly defined handling of the samples, we conducted a systematic study of this PL following the known adsorption and desorption behavior of water on silica and other oxides.[20–23] The PL from silanol groups is the broad feature in Fig. 1 with the maximum intensity around 2.8 eV.

We shall now briefly summarize the evidence: The open circles in Fig. 1 show the PL from nc-Si/SiO$_2$ nanocomposites prepared by oxidation of nc-Si films (deposited by plasma CVD at 82 °C) in pure oxygen at 870 °C for 3 min, and subsequently treated in ultrapure boiling water for 5 h followed by annealing in forming gas at 350 °C for 1.5 h.[8] The red full squares is the PL from finely dispersed SiO$_2$, and the open black diamonds is the PL from Al$_2$O$_3$, both oxides treated in water and forming gas in the same way as the nc-Si/SiO$_2$ nanocomposite (see Fig. 2 in Ref. 8). When the treatment of nc-Si/SiO$_2$ nanocomposites in oxygen, water, and forming gas has been repeated several times so that nc-Si was fully oxidized to SiO$_2$, the PL at about 1.5–1.6 eV (which originates from nc-Si/SiO$_2$ nanocomposites with the NBOHC) vanished, and only that from the silanols persisted.[8] The PL from silanols (full magenta squares in Fig. 1) and alanols (open diamonds) showed polarization memory (see Fig. 9 in Ref. 8), indicating that the photon absorption and emission occurred from the same sites, i.e.,

$\equiv$Si–O–H and $\equiv$Al–O–H groups. It should be pointed out the PL from alanols has been reported by Jeziorowski and Knözinger already in 1997.[24] The PL from silanols and alanols showed also similar behavior upon annealing in forming gas after the SiO_2 and Al_2O_3 samples have been boiled in ultrapure water: after the treatment in water, i.e., without any annealing, the PL was very weak because the physisorbed water was covering the $\equiv$Si–O–H and $\equiv$Al–O–H groups. Upon annealing in forming gas above 120 °C, where desorption of the physisorbed water begins,[20] the PL intensity strongly increased and reached a maximum after annealing at about 450 °C. Upon further annealing at higher temperature, the PL intensity deceased due to desorption of the chemisorbed OH groups until it vanished after annealing above about 600–650 °C where all OH groups were removed (see Fig. 5 in Ref. 8). The measured decay time of this PL has been in the range of several nanoseconds, comparable with the decay time of the laser available to us at that time (see Fig. 6 and Table 1 in Ref. 8).

Although the sample preparation and handling has been done under ultrapure conditions as used in the semiconductor technology (see Ref. 8, Sec. 2), we wanted to be sure that the PL is not due to some impurities, because organosilicon compounds, which might be formed by interaction of Si with hydrocarbons from air, show very intense PL of high quantum efficiency (see, e.g., Refs. 25 and 26). Therefore, we used several silica glasses of high purity, such as Pursil and synthetic Spectrosil, as well as Corning 7059 for comparative study. The PL obtained after the same treatment as described above showed an almost identical spectral distribution (see Fig. 1 in Ref. 19) behavior upon annealing in forming gas at increasing temperature (see Fig. 3 in Ref. 3 and Fig. 3 in Ref. 19) and fast decay time (unpublished results of our group from 1995/1995) as the PL from silanols and alanols shown in Fig. 1. Furthermore, the same PL has been obtained from ultrapure Al foil, which has been boiled in ultrapure water and annealed in forming gas. Similar PL has also been obtained from ZnO and PbO_2,[8] spark-processed Si,[27] and nc-Si/SiO_2 nanocomposites doped with tungsten.[28]

III. DISCUSSION AND CONCLUSIONS

To summarize, the so called "red" PL from nc-Si/SiO_2 nanocomposites with maximum intensity at photon energy around 1.6 eV is a combined process: the absorption of the excitation light occurs in the Si nanocrystals and it increases with decreasing crystallite size (Fig. 2 of Ref. 2) following the theoretically calculated transition probability between the ground and excited states with the formation of photogenerated electron-hole pairs [Fig. 4(a) in Ref. 15]. However, the electrons and holes are fast trapped in defect sites in the SiO_2 matrix from where the PL with a spectral distribution independent of the crystallite size of the nc-Si occurs. NBOHC are the radiative centers identified in our samples.[17] Porous Si and Si nanowires passivated by covalently bonded hydrogen show blue shift of the PL with decreasing crystallite size, as expected from the increase of the bandgap (see Fig. 2). (Note that Wolkin et al. did not

determine the diameter of the porous silicon but adjusted the data (red crosses) to the theoretical calculations of Delerue et al. for Si nanocrystals (dotted line), whereas the results of Zheng et al. (red asterisk) apply to Si wires, which have more in common with the P-Si than the Si nanocrystals considered in the calculations of Delerue. The band gap of our Si nanocrystals imbedded in the SiO_2 matrix has been determined from the measured excitation spectra.[29] Assuming an indirect band gap (i.e., extrapolating the root square of the product to the intensity of the PL and excitation energy, for details see Ref. 29), one obtains results shown in Fig. 2 as blue full symbols. These data agree very well with the calculations down to crystallite size of about 2 nm, becoming smaller than the theoretical values for a smaller crystallite size. Assuming a direct bandgap (open triangles in Fig. 2) results in a good agreement with theoretical calculations for crystallite size ≤ 2 nm, where the scattering on the surfaces of the nanocrystals causes the bandgap of silicon to become pseudodirect. Let us mention that also the calculations of Delley and Steigmeier[16] show a very similar dependence as those of Delerue et al.[30] Of course, the assumption of direct band gap yields incorrect results for larger crystallite size, as seen in Fig. 2.

The "green/blue" PL from O-H groups with a maximum intensity around 2.8 eV has been found in a number of different oxides including SiO_2, Al_2O_3, and others. Its pronounced polarization dependence and fast decay indicate that the silanol and alanol groups are the centers where photon absorption and emission occur. The dependence of the PL of the heavily hydrated samples on the annealing temperature in forming gas agrees with the known reversible adsorption and desorption of water on silica and alumina. The fact that the same PL has been observed from pure silica glasses exposed to the same treatment underlines that this PL is not associated with silicon nanocrystals.

[1]S. L. Weeks, R. P. Chaukulkar, P. Stradins, and S. Agarwal, J. Vac. Sci. Technol. A **32**, 050604 (2014).
[2]M. Rückschloss, B. Landkammer, and S. Veprek, Appl. Phys. Lett. **63**, 1474 (1993).
[3]H. Tamura, M. Rückschloss, T. Wirschem, and S. Veprek, Thin Solid Films **255**, 92 (1995).
[4]S. Veprek, F.-A. Sarott, and Z. Iqbal, Phys. Rev. B **36**, 3344 (1987).
[5]S. Veprek and Th. Wirschem, in *Handbook of Optical Properties, Vol. II, Optics of Small Particles, Interfaces, and Surfaces*, edited by R. E. Hummel and P. Wißmann (CRC, Boca Raton, FL, 1997), pp. 129–143.
[6]G. Schumicki and P. Seegebrecht, *Prozesstechnology* (Springer-Verlag, Berlin, 1991), p. 163 (in German).
[7]S. Veprek, H. Tamura, M. Rückschloss, and Th. Wirschem, Mater. Res. Soc. Symp. Proc. **345**, 311 (1994).
[8]M. Rückschloss, Th. Wirschem, H. Tamura, G. Ruhl, J. Oswald, and S. Veprek, J. Lumin. **63**, 279 (1995).
[9]M. Rückschloss, O. Ambacher, and S. Veprek, J. Lumin. **57**, 1 (1993).
[10]M. V. Wolkin, J. Jorne, P. M. Fauchet, G. Allan, and C. Delerue, Phys. Rev. Lett. **82**, 197 (1999).

[11]D. D. D. Ma, C. S. Lee, F. C. Au, S. Y. Tong, and S. T. Lee, Science **299**, 1874 (2003).

[12]Y. Zheng, C. Rivas, R. Lake, K. Alam, T. B. Boykin, and G. Klimeck, IEEE Trans. Electron Devices **52**, 1097 (2005).

[13]R. Rurali, B. Aradi, Th. Frauenheim, and A. Gali, Phys. Rev. B **76**, 113303 (2007).

[14]M. L. Mastronardi, F. Maier-Flaig, D. Faulkner, E. J. Henderson, Ch. Kübel, U. Lemmer, and G. A. Ozin, Nano Lett. **12**, 337 (2012).

[15]S. Veprek, Solid State Phenom. **51–52**, 225 (1996).

[16]B. Delley and E. F. Steigmeier, Phys. Rev. B **47**, 1397 (1993).

[17]S. M. Prokes, W. E. Carlos, S. Veprek, and Ch. Ossadnik, Phys. Rev. B **58**, 15632 (1998).

[18]Z. Hajnal, P. Deák, Th. Köhler, R. Kaschner, and Th. Frauenheim, Solid State Commun. **108**, 93 (1998).

[19]H. Tamura, M. Rückschloss, Th. Wirschem, and S. Veprek, Appl. Phys. Lett. **65**, 1537 (1994).

[20]The first stage is chemisorption of H_2O on SiO_2 surface according to $2Si + H_2O \rightarrow 2 \equiv Si\text{-}O\text{-}H$, followed by physisorption of H_2O on these polar sites. Upon annealing, the physisorbed H_2O desorbs above 100–130 °C, leaving the chemisorbed $\equiv Si\text{-}O\text{-}H$ sites stable up to >450 °C where their desorption begins and is completed at about 600 °C. Of course the time of the annealing also plays a role. For more detail see Refs. 21–23.

[21]R. K. Iler, *The Chemistry of Silica: Solubility, Polymerization, Colloid and Surface Properties and Biochemistry* (Wiley, New York, 1979).

[22]L. T. Zhuravlev, Pure Appl. Chem. **61**, 1969 (1989).

[23]J. M. J Vankan, J. J Ponjeé, J. W De Haan, and L. J. M. Van de Ven, J. Colloid Interface Sci. **126**, 604 (1988).

[24]H. Jeziorowski and H. Knözinger, Chem. Phys. Lett. **51**, 519 (1977).

[25]R. D. Miller and J. Michl, Chem. Rev. **89**, 1359 (1989).

[26]Y. Kanemitsu, Phys. Rep. **263**, 1 (1995).

[27]S. Veprek, Th. Wirschem, J. Dian, S. Perna, R. Merica, M. G. J. Veprek-Heijman, R. Heinecke, and V. Perina, Thin Solid Films **297**, 171 (1997).

[28]S. Veprek, M. Rückschloss, Th. Wirschem, B. Landkammer, M. Fuss, and X. Lin, Appl. Phys. Lett. **67**, 2215 (1995).

[29]Th. Wirschem, "Luminescence of nanocrystalline silicon and related materials (in German)," Ph.D. thesis (Technical University Munich, 1996); Th. Wirschem and S. Veprek (1995/1996) (unpublished).

[30]C. Delerue, M. Lannoo, and G. Allan, J. Lumin. **57**, 249 (1993).