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Silicon nanocrystals prepared by plasma enhanced chemical vapor deposition: Importance of parasitic oxidation for third generation photovoltaic applications

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We report on an in-situ oxidation effect during annealing of SiO2/SiO1.0N0.23 multilayers prepared by plasma enhanced chemical vapour deposition (PECVD). This in-situ oxidation leads to an undesired growth of the tunneling oxide and also affects the silicon nanocrystal (SiNC) size control, i.e., a NC shrinkage. The origin of this oxidation is identified to be a “quasi-wet” oxidation by O–H groups incorporated in the PECVD-SiO2 barrier layers. By varying the thickness of the PECVD-SiO2 layer underneath a single SiO1.0N0.23 layer, the extent of NC oxidation is tuned. The shrinkage of SiNCs is proven by a blueshift of the photoluminescence peak position as well as by transmission electron microscopy. © 2012 American Institute of Physics. [http://dx.doi.org/10.1063/1.4766284]

Various kinds of potential applications have been reported for silicon nanocrystals (SiNCs) embedded in silicon dioxide in recent years such as microelectronic and optoelectronic devices,1–3 high efficiency “all-silicon” solar cells,4–6 image sensors or photodiodes, and SiNC based non-volatile memories.7–10 However, a precise control of the Si quantum dot size and thereby the quantum confinement energy as well as a good interface quality are essential for such devices. Chemical vapor deposition (CVD) techniques seem to be the most suitable way to produce such devices. Especially, the plasma-enhanced chemical vapor deposition (PECVD) meets all the requirements of MOS technology and offers many advantages in terms of film quality, reproducibility, and flexibility. One additional advantage of the PECVD technology, in particular, for solar cell applications is the fact that it is easily up-scalable. Large PECVD deposition systems already facilitate thin film PV modules such as a-Si solar cells.11 The major step towards precise quantum dot size control was done by the SiNC fabrication via the SiO2/SiO2 superlattice (SL) approach,12 where the SiNC size control is achieved by limiting the Si diffusion and Si clustering to a thin sub-oxide layer by adjacent SiO2 barriers. Recently, the SL approach was also demonstrated using PECVD grown SiO1.0N0.23 thin films.13,14 However, in particular, for high efficiency third generation PV, the width of the SiO2 barriers as well as the SiNC size have a tremendous impact on the electrical transport properties, e.g., via miniband formation.15,16 In this study, we reveal the influence of parasitic O–H groups that are inevitably incorporated in the PECVD grown layers on the final multilayer structure. We present a detailed study about the origin of an undesired tunneling oxide growth at the bulk Si interface as well as about a self organized quasi-wet in-situ oxidation of the SiNCs during annealing resulting in a decrease of SiNC diameters. With quadrupole mass spectrometry (QMS), we will prove the presence of O–H groups in the PECVD grown layers and together with transmission electron microscopy (TEM), photoluminescence (PL) spectroscopy, and a dedicated control experiment we will verify our thesis about a self organized quasi-wet in-situ oxidation of the barriers as well as of the SiNCs.

Layer stacks consisting of 3 layers (SiO2 buffer layer, SiO1.0N0.23 crystallization layer, and SiO2 capping layer) were deposited on wet chemically cleaned n-type (100)-Si substrates using PECVD. The thickness of the SiO2 capping layer was kept constant at 5 nm. For the SiO1.0N0.23 layer (containing the SiNCs after annealing), a constant thickness of 5 nm was used. The SiO2 buffer layer thicknesses were chosen to be 5, 20, 50, and 100 nm, respectively. Please note that the layer thickness was solely controlled by varying the deposition time while keeping the other parameters of the recipe constant (such as gas flow ratio, plasma power, and temperature), i.e., the composition of the SiO2 buffer layer is identical for all samples. As control experiment, the SiO2 buffer layers of 4 additional samples with the same buffer layer thicknesses as the other samples were pre-annealed at 1150 °C for 4 h in high purity N2. For these 4 control samples, the SiO1.0N0.23 layer and the SiO2 capping layer were deposited afterwards. Further details of the sample preparation method are given in elsewhere.13 Subsequently, all samples were annealed in a quartz tube furnace at 1100 °C for 1 h in high purity N2. For these 4 control samples, the SiO1.0N0.23 layer and the SiO2 capping layer were deposited afterwards. Further details of the sample preparation method are given in elsewhere.13 Subsequently, all samples were annealed in a quartz tube furnace at 1100 °C for 1 h in high purity N2. For these 4 control samples, the SiO1.0N0.23 layer and the SiO2 capping layer were deposited afterwards.

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PL spectra were measured for all samples at room temperature with a LN2-cooled CCD camera attached to a single grating monochromator using a HeCd laser (3.8 eV line) as excitation source. All spectra were corrected for the spectral response of the setup. The thickness and the dielectric function of the films were measured at room temperature using variable angle spectroscopic ellipsometry in an energy range of 1.1–4 eV. For cross sectional TEM, imaging a Philips CM-20 electron microscope operated at 200 kV was used. The TEM specimen was prepared by mechanical thinning followed by argon ion milling to electron transparency. The plane-view energy filtered TEM (EFTEM) analysis was performed using an image corrected FEI Titan 80–300 operated at 300 kV, equipped with a Gatan Tridiem Imaging Filter and a US1000 slow-scan CCD camera. EFTEM images were acquired with a 5 eV energy slit centred around an energy loss of 17 eV (i.e., the Si plasmon loss energy). Image noise was reduced after background correction using the non-linear anisotropic diffusion implemented in IMOD.\textsuperscript{17} For plane-view TEM, the sample structure was deposited on a special Si-TEM grid with a free standing silicon membrane of 5 nm thickness (SimPore, USA).

First of all, we want to motivate the study of the in-situ quasi-wet oxidation process by demonstrating its deleterious effect on the tunnelling oxide thickness. Fig. 1 shows TEM images of two SL-samples actually prepared for measurements of the charge transport between NC layers. Both samples consist of 4 bilayers with the same NC-size but different SiO\textsubscript{2} barrier thicknesses: 2 nm (Fig. 1(a)) and 4 nm (Fig. 1(b)). From the electrical measurements, we deduced that the thickness of the first SiO\textsubscript{2} layer at the bulk silicon interface seems to be thicker than expected from the selected/ chosen deposition rates. As confirmed by the TEM images shown in Fig. 1, the initial SiO\textsubscript{2} layers (on the Si wafer) of both samples are approximately 50% thicker than nominally deposited, i.e., 3 nm in Fig. 1(a) and 6 nm in Fig. 1(b). All the other layers (the SiO\textsubscript{2} barriers between NC layers as well as the SiO\textsubscript{1.0N0.23} layers) have exactly the nominally deposited thicknesses for both samples. Since the deposition conditions are identical for each stoichiometry, we can exclude inhomogeneities during the PECVD layer growth. It seems to be rather a subsequent oxidation causing the additional interface growth. However, neither the silicon substrate nor the annealing atmosphere (high purity N\textsubscript{2} in a pre-evacuated furnace) contains oxygen or oxidizing O–H groups in sufficiently high concentrations. The only source of oxidizing species can be the SiO\textsubscript{2} itself. To verify this assumption, we carried out effusion experiments with thick films of the corresponding stoichiometries and a bare silicon control sample as described in the experimental details. The QMS signal of both, the SiO\textsubscript{2} and the SiO\textsubscript{1.0N0.23} single layer films (Fig. 2(a)), was analyzed as a function of the temperature for 18 amu (corresponding to H–O–H) and 17 amu (corresponding to O–H). From the bare reference silicon sample, we could not observe any QMS signal. Thus, the substrate can be excluded as oxidizer and is, therefore, not shown in Fig. 2. For the other samples, the experiment shows that there is “water” effusing from the SiO\textsubscript{2} as well as from the Si-rich oxinitride (SRON). However, there is a much higher amount

![FIG. 1. Bright field TEM images of (a) 4 bilayers of SiO\textsubscript{2}/SiO\textsubscript{1.0N0.23} (2 nm/3.5 nm) capped with 2 nm SiO\textsubscript{2} and (b) 4 bilayers of SiO\textsubscript{2}/SiO\textsubscript{1.0N0.23} (4 nm/3.5 nm) capped with 4 nm SiO\textsubscript{2}. The dashed lines indicate the interfaces between the individual sublayers.](image)

![FIG. 2. (a) QMS signal for SiO\textsubscript{2} (black lines) and Si\textsubscript{1.0N0.23} (red lines) versus sample temperature for the masses 18 amu (corresponding to H–O–H) and 17 amu (corresponding to O–H). From the bare reference silicon sample, we could not observe any QMS signal. Thus, the substrate can be excluded as oxidizer and is, therefore, not shown in Fig. 2. For the other samples, the experiment shows that there is “water” effusing from the SiO\textsubscript{2} as well as from the Si-rich oxinitride (SRON). However, there is a much higher amount](image)
of water effusing from the SiO$_2$ compared to the SRON. The mean signal for the SiO$_2$ layer is three times higher than that for the SRON material. The stoichiometric SiO$_2$ layers are obviously saturated with water, whereas the suboxides seem to getter O–H groups. The ratio $\eta = (17 \text{ amu}/18 \text{ amu})$ results in a rather constant value of around $\eta_{\text{SRON}} \approx 0.23$ for the SiO$_{1.0}$N$_{0.23}$ layer over the whole temperature range (please note that $\eta \approx 0.23$ is the typical value observed for pure water in a quadrupole mass spectrometer due to its fragmentation pattern). In contrast to that, we measure a slightly higher $\eta$ value of $\eta_{\text{SiO}_2} \approx 0.32$ for sample temperatures of $T_S \geq 550^\circ \text{C}$ for the stoichiometric SiO$_2$ film (Fig. 2(b)). Thus, there is a higher amount of O–H groups effusing from the SiO$_2$ layers compared to the SRON. Nevertheless, H–O–H as well as O–H are able to oxidize silicon. Please note, no other QMS signals of atomic or molecular oxygen could be observed during the effusion experiments. The thickness of the SiO$_2$ barrier has a tremendous impact on the electrical transport properties of the nanocrystal stack (the current is reduced 5 orders in magnitude per nanometer SiO$_2$). Hence, it is mandatory to take the presence of oxidizing species in the PECVD grown SiO$_2$ into account and to compensate the effect of barrier growth by adjusting the deposition parameters. To investigate the influence of the oxidation on the nanocrystal growth, we designed an experiment in which we varied the thickness (5, 20, 50, and 100 nm) of the SiO$_2$ buffer layer underneath a single SiO$_{1.0}$N$_{0.23}$ layer of constant thickness (5 nm) capped with 5 nm of SiO$_2$. For comparison, we prepared an additional control sample set with the same sample structure but with a pre-annealed buffer layer (1150$^\circ$C for 4 h in high purity N$_2$) to ensure that the SiO$_2$ interface does not contain water anymore. In Fig. 3, we show the results of the PL investigations of both sample sets. It is well established that the PL peak position of SiNCs shifts towards higher emission energies due to quantum confinement for decreasing sizes.\cite{12,13,18,19} As shown in Fig. 3(a), we observe indeed a PL blue shift from 850 to 720 nm for the standard annealed samples with increasing SiO$_2$ buffer layer thickness from 5 to 100 nm. However, the comparison of the standard annealed samples with the pre-annealed control samples (Fig. 3(b)) reveals a huge difference. The PL peak position for the standard annealed samples is a strongly decreasing function with increasing buffer layer thickness, whereas the PL peak position of the control samples is rather an oscillating function around a constant value. This is a clear indication of a reduction of the NC sizes by a quasi-wet in-film oxidation caused by water incorporated in the SiO$_2$ buffer layer for the not pre-annealed samples. The oscillation of the peak position around a certain centre wavelength $\lambda_0$ for the pre-annealed samples is solely an optical effect depending on the thickness and the refractive index of the total layer stack. It can be calculated using transfer matrix method considering emitting dipoles within the layer stack as shown elsewhere.\cite{20,21,22} It shows that the peak position is not affected by oxidation anymore if the buffer layer is pre-annealed. To verify the oxidation process, we used TEM for two standard annealed samples with buffer sizes of 10 nm (Fig. 4(b)) and 50 nm (Fig. 4(a)), respectively. From the cross-sectional TEM image in Fig. 4(a), we can estimate a SiNC size of 3.5 ± 0.5 nm for standard annealed sample with a buffer layer size of 50 nm. From the plane-view TEM image in Fig. 4(b), the SiNC size can be estimated to be 4.5 ± 0.4 nm for the standard annealed sample with a buffer layer size of 10 nm. Thus, the NC diameter is reduced by approximately 1 nm if the buffer layer thickness is increased from 10 to 50 nm. Unfortunately, plane-view TEM imaging of the sample with 50 nm buffer SiO$_2$ is inhibited by the insufficient electron transparency of the specimen accompanied by a virtually total loss in contrast. Thus, we cannot rule out some error in estimating the SiNC size from the cross-sectional image caused by nanocrystals possibly located right behind each other. However, in this case, the actual size of the SiNCs would be rather overestimated which, if applicable, would just strengthen the apparent NC shrinking effect.

Electrical measurements on PECVD grown superlattices consisting of stoichiometric silicon oxide (SiO$_2$) and silicon rich oxide (SiO$_{1.0}$N$_{0.23}$) suggested an undesired growth of...
the SiO2 tunneling oxide barrier adjacent to the silicon substrate during annealing. TEM investigations of these samples confirmed this assumption. The quadrupole mass spectrometric investigations of thick films of the respective stoichiometries revealed that the PECVD grown layers contain a considerable amount of O–H groups which are effusing during annealing. We could show that, in particular, the stoichiometric SiO2 has a high oxidation potential caused by incorporated O–H groups. This leads to an oxidation at the bulk silicon interface and thereby to a further growth of the tunneling oxide. In our case, the tunneling oxide thickness increased by approximately 50% compared to its nominal thickness during annealing. By varying the SiO2 buffer oxide thickness underneath a single layer of sub-stoichiometric SiO1.0N0.23, we could show that the photoluminescence peak position is drastically shifting towards higher energies with increasing SiO2 buffer layer thickness. This undoubtedly indicates a shrinkage of the silicon nanocrystals due to a quasi-wet in-situ oxidation caused by the water incorporated in the oxide films. The degree of this oxidation is strongly dependent on the SiO2 buffer layer thickness, i.e., the amount of available O–H groups. To exclude the origin of this behavior from another effect, a control set of similar sample structure but pre-annealed buffer layer (not containing O–H groups anymore) was prepared. The PL of this sample set proved our assumption since the PL peak position is not blue shifting anymore. Finally, TEM investigations of the “self-oxidized” samples revealed doubtless evidence of the oxidation. For a SiO2 buffer layer thickness of 10 nm, the SiO2 tunneling oxide thickness is not negligible (50% additional growth compared to the nominal thickness) and therefore has to be taken into account in device design.

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