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We investigate the influence of layer thicknesses and interface modifications on the fundamental electronic gap of Si/SiO_2 multilayers by a combined *ab initio* calculation and photoluminescence (PL) analysis. For the band gap calculations different Si/SiO_2 interface models are studied. Experimentally investigated multiple quantum wells are prepared by remote plasma-enhanced chemical vapor deposition and rapid thermal annealing. The well-width dependence of the band gap obtained from PL measurements is much weaker than found in previous studies. This sublinear variation is in accordance with simulated electronic band gaps for hydrogen-free Si/SiO_2 interfaces. The presence of hydrogen at the interfaces enforces the confinement effect for the band gap. Materials involved: nanocrystalline silicon, amorphous silica, β-cristobalite silica, and Si/SiO_2 interface. © *2007 American Vacuum Society.* [DOI: 10.1116/1.2779040]

I. INTRODUCTION

In recent years Si nanostructures have gained major interest due to their enhanced light emission properties.[1,2] In addition, the increase of the band gap energy due to quantum size effects makes this material suitable for the realization of highly efficient Si-based tandem solar cells.[3] These third-generation solar cells comprise at least two absorber materials with different energy gaps, leading to dramatic reductions in hot carrier losses compared to conventional bulk Si solar cells.[4] Regarding this application, a comprehensive understanding of the quantum size effects for Si-based quantum wells is needed. One way toward such understanding is the comparison of measured band gaps of Si/SiO_2 quantum wells with respective results of *ab initio* calculations.

Prototypical Si-based systems to study quantum-size effects are short-period Si/SiO_2 multiple quantum wells (MQWs). Being type-I heterostructures, electrons and holes are strongly confined by the SiO_2 barriers within the Si quantum wells. MQWs have been fabricated by molecular-beam epitaxy and chemical vapor deposition. They exhibit an enhanced luminescence in the visible or infrared part of the spectrum. Due to confinement a blueshift is observed when the thickness of the Si layers is reduced from 6 to 1 nm.[5–8] However, their optical properties are considerably influenced by the crystalline structure and the perfection/stoichiometry of the interfaces to the SiO_2 barriers. The homogeneity of the prepared Si layers or the formation of Si nanocrystallites in them determines the resulting one- or three-dimensional confinement. The actual properties of the layered Si/SiO_2 systems depend remarkably on the film deposition method and their subsequent treatment.[9–11] For the structural and electronic properties a significant influence of the interface has been demonstrated by first-principles calculations.[12–14]

In this article, we study the quantum confinement of electrons and holes in stacks of ultrathin Si/SiO_2 layers versus Si layer thickness by a combination of theoretical and experimental methods. From photoluminescence (PL) spectra, taken for a series of samples with different well widths, we determine the dependence of the electronic band gap on the Si-layer thickness. The influence of the interface structure and stoichiometry on this dependence is investigated by first-principles calculations for a variety of interface models.

II. SAMPLE FABRICATION AND PL MEASUREMENTS

The Si/SiO_2 MQWs are fabricated by means of remote plasma-enhanced chemical vapor deposition (RPECVD). Rapid thermal annealing (RTA) is applied for 30 s in an N_2 atmosphere at 1100 °C.[11,15] The crystallization state of the MQW layers is investigated by cross-sectional high-resolution (HR) transmission electron microscopy (TEM). In the bright-field TEM image (see Fig. 1) the resulting Si and SiO_2 layers are compact, with relatively sharp interfaces. Due to the RTA procedure a recrystallization of the Si layers occurs. The HRTEM analysis shows that the resulting QW layers tend to be polycrystalline or nanocrystalline and not to be homogeneous. However, the crystalline Si grains touch each other and are embedded in remaining amorphous Si. Nevertheless, the Si layers obtained after RPECVD and RTA justify to use a quantum well model instead of a quantum dot

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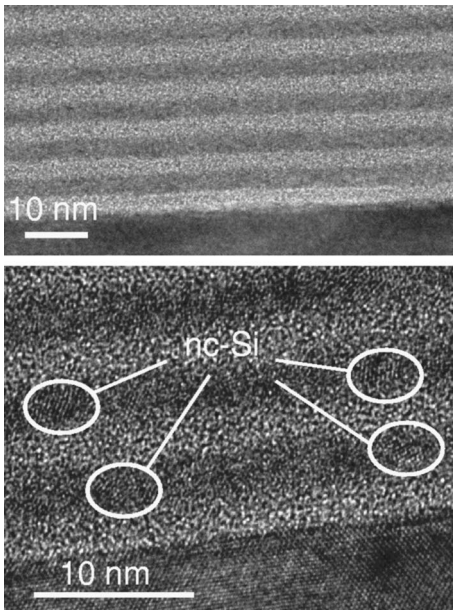

FIG. 1. Bright-field TEM image (upper part) and HRTEM analysis (lower part) of a stack of ten Si/SiO_2 periods (annealed). The nominal thickness of the Si quantum wells amounts to 4 nm while the SiO_2 barriers are 3 nm thick.

description in the band structure calculations: First, the characteristic lateral length scale of the grains (4–8 nm) is larger than the layer thickness, and second, the large band gap of the SiO_2 barriers leads to at least eight times larger potential barrier heights compared to the low energy barrier in lateral direction formed by grain boundaries to the remaining amorphous Si.[16,17]

Low-temperature photoluminescence measurements under 405 nm laser excitation[15] lead to the spectra in Fig. 2. Despite the strong thickness variation of the Si layers from 4 to 1 nm, the emission bands mainly appear in the infrared spectral region. The maxima are blueshifted with respect to the bulk Si band gap from 1.2 to 1.6 eV. This is in clear contrast to previous studies with emission in the visible spectral range.[6,7] The reduced confinement effects in our samples

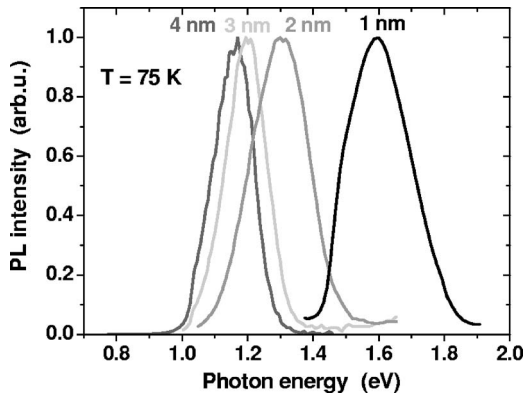

FIG. 2. Normalized PL spectra of Si/SiO_2 MQW structures at 75 K for varying thicknesses between 4 and 1 nm of the Si quantum wells. The thickness of the SiO_2 barrier layers has been fixed at 3 nm.

indicate a better crystallinity of the Si QW layers, or at least more asymmetrically extended Si grains. Another argument is the only slight increase of the width of the emission bands in the PL spectra with decreasing QW thickness. In the context of one-dimensional confinement this effect may be interpreted as a result of the Heisenberg uncertainty principle leading to a broader energy distribution as a consequence of the carrier wave functions being confined in ultrathin QW structures. The bandwidths are smaller than expected for an ensemble of small Si nanocrystallites with a certain distribution of their diameter. Indeed, in addition to higher peak energies, also larger peak widths have been observed in previous studies[6,7] for nominally the same layer thickness.

III. CALCULATIONAL APPROACH

To determine the thickness dependence of the band gaps of the Si/SiO_2 MQW structures *ab initio*, one has to model realistic layered systems combining more or less crystalline Si layers with almost amorphous SiO_2 barriers via a transition region, the Si/SiO_2 interface, on a nanometer length scale. Unfortunately, the true chemistry and geometry of the prepared Si/SiO_2 interfaces are not known. For that reason, the theoretical studies are limited to model interfaces. Following the suggestions of previous studies we model the amorphous SiO_2 by the crystalline β-cristobalite modification. This seems to be a good approximation to study carrier confinement effects since β-cristobalite leads to almost the same potential barrier heights for electrons and holes as the amorphous silica.[18] Moreover, crystalline silica has been observed at the Si/SiO_2 interface.[10,19] The advantage of this approach is that the lattice parameter of β-cristobalite is approximately $\sqrt{2}$ times that of Si. Hence, a rather perfect match follows applying the β-cristobalite structure along the diagonal of the (001) surface unit cell of Si with a slight tensile biaxial strain on SiO_2. This leaves every second interface Si atom with two dangling bonds. Among the various possibilities for passivation we study the four models shown in Fig. 3, leading to rather well ordered, abrupt, interfaces with nominal extents of 0.2–0.4 nm and representing different interface dipoles: (i) the double-bond model[20] (DBM) with Si dangling-bond saturation by addition of a single double-bonded oxygen atom (Si=O), (ii) the bridging-oxygen model[21] (BOM) with a substitutional O atom in the topmost Si layer (Si-O-Si), and (iii)/(iv) the hydroxyl/hydrogen model (HXM/HGM) where each Si dangling bond is saturated by a hydroxyl group or a hydrogen atom (Si-OH/Si-H), respectively.[22]

The earlier-described stacked geometries for the Si/SiO_2 MQW structures are allowed to fully relax, i.e., to displace the atomic coordinates in order to obtain a local minimum on the total energy surface. As a consequence, the vertical regions with distorted Si and β-cristobalite SiO_2 become more extended compared to the starting geometries. Thereby, the atomic relaxation corresponds to the effect of repeated application of RTA on the structures studied experimentally. Because of the high migration probability,[23] we expect that the amount of hydrogen will be strongly reduced in the resulting

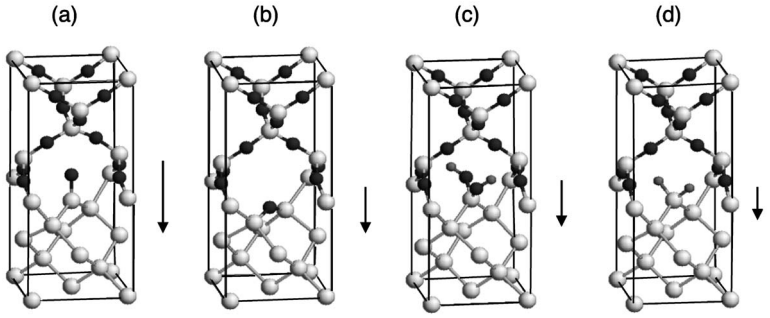

FIG. 3. The four interface model structures considered in the present *ab initio* study: (a) DBM, (b) BOM, (c) HXM, and (d) HGM. The light gray balls represent Si, the dark gray ones represent O, and the medium gray ones represent H atoms. The resulting interface dipole is characterized by an arrow with a certain direction and length.

interfaces despite its presence in the as-grown RPECVD-deposited samples. Nevertheless, the modeling of hydrogen-containing interface models (HXM/HGM) may be interpreted as the description of other chemical species that passivate Si dangling bonds in the interface region.

The computations are based on *ab initio* density functional theory (DFT) and local density approximation (LDA) using the Vienna Ab-initio Simulation Package, VASP.[24] Pseudopotentials are generated in accordance to the projector-augmented wave method. The kinetic-energy cutoff for the plane-wave expansion is chosen to be 30 Ry. The model structures are relaxed until the Hellmann–Feynman forces almost vanish (below 10 meV/Å). Since DFT-LDA is a ground-state theory, their electronic energy eigenvalues do not correctly describe the excitation energies of electrons and holes. For instance, the bulk Si value of the fundamental indirect gap is found as 0.44 eV. Including many-body quasiparticle effects[25] the correct experimental value is however nearly obtained. Such quasiparticle corrections can also be computed for the optical transitions in SiO_2.[26] However, for the MQW structures studied here with up to 100 atoms in the supercell the computation of such many-body corrections are extremely time consuming. Moreover, here only the general trend of the thickness dependence of the band gap is important for drawing conclusions. Therefore, we focus our attention not to obtain the absolute gap values but their thickness variation. For that reason we present both the calculated and measured gaps normalized to the respective bulk Si value. This presentation corresponds implicitly to the assumption that the thickness dependence of the quasiparticle gap opening scales similarly to that of the DFT-LDA gap. We have checked this approach by calculating the quasiparticle shifts within an approximate treatment of the quasiparticle excitation aspect using a model dielectric function derived as a thickness-weighted average of the Si and SiO_2 values.[27]

IV. RESULTS AND DISCUSSION

The electronic-structure results have been derived for SiO_2 barriers of $d_{SiO_2}=1.41$ nm (i.e., about two lattice constants of biaxially strained β-cristobalite SiO_2) and thicknesses of the Si QW layers $d_{Si}=1.08$, 1.62, 2.16, 3.24, and 4.32 nm (i.e., multiples of the calculated Si equilibrium lattice constant). The fundamental gap values $E_g(d_{Si})$ resulting for the four interface models and normalized to the value of bulk Si are plotted in Fig. 4 versus the QW thickness d_{Si}. They are compared with corresponding measured values derived as peak positions of PL spectra (normalized to the experimental gap value at low temperatures, 1.17 eV). The calculated band gaps have been determined as the smallest energy distances between occupied and empty bands at the Γ point of the MQW structure. The small energy deviations due to the small displacements of the valence band maximum out of the Γ point have been omitted. By investigating selected MQW structures with thicker SiO_2 layers we have checked that the thickness of the SiO_2 barriers is of minor influence on the MQW gap. A silica layer with $d_{SiO_2}=1.41$ nm already avoids the tunneling of wave functions through the barriers.

The $E_g(d_{Si})$ curves calculated for interfaces with and without the presence of hydrogen show a significant difference with respect to their behavior at small Si layer thicknesses. Expressed as a power law dependence $E_g \propto d_{Si}^{-n}$, one finds for the hydrogen-free interfaces DBM and BOM an exponent $n<1$. The graph for BOM is shifted toward higher energies, indicating an overall stronger confinement. On the other hand, the thickness variations calculated for the hydrogen-containing interfaces HXM and HGM show a steep increase for d_{Si} approaching small thicknesses of 1 nm. This trend is also confirmed by a description of the quasipar-

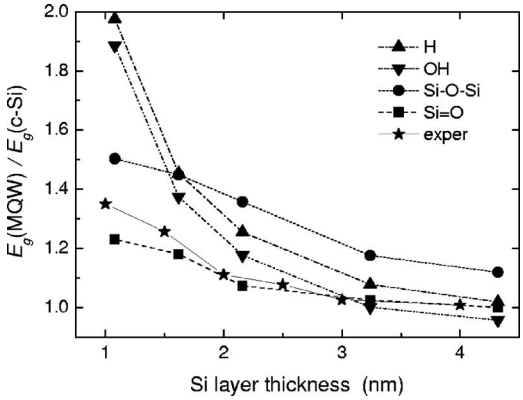

FIG. 4. Comparison of calculated and measured lowest energy gaps of Si/SiO_2 MQW structures vs the thickness d_{Si} of the Si QWs, normalized to the respective bulk value of *c*-Si. The values computed for four interface models and $d_{SiO_2}=1.41$ nm are indicated by the symbols/line types: squares/dashed (DBM), circles/dotted (BOM), down triangles/double-dot-dashed (HXM), and up triangles/dot-dashed (HGM). The gap energies measured as peak maxima of PL spectra for $d_{SiO_2}=3$ nm are given by asterisks/full line. All lines are just a guide to the eye.

ticle excitation aspect using a model screening.[27] Overall, the HXM and HGM curves exhibit a similar strong gap increase as follows from the effective mass theory for rectangular potential wells (not shown in Fig. 4 for clarity) with a larger exponent tending toward $n \approx 2$, in contrast to the hydrogen-free interfaces with $n \lesssim 1$.

Most important, the measured PL peak positions show a similar weak thickness dependence as the $E_g(d_{Si})$ curves calculated for the hydrogen-free interfaces DBM and BOM. Also for the measured values we find an exponent $n < 1$, in clear contrast to observations of $n \approx 2$ for Si layers dominated by nanocrystallites.[6,7] Incidentally, the gaps computed for the DBM even coincide with the measured values. However, the good agreement between the DBM graph and the PL findings does not mean that the double-bond model solely characterizes the essential features of the prepared Si/SiO_2 interfaces. The magnitude and the thickness dependence of the measured data may be interpreted as the consequence of various structural and chemical interface elements being simultaneously present. Moreover, excitonic binding energies as well as internal compressive strain[28] may lead to deviations between the "true" band gap and the measured PL peak energies. For bulk Si the exciton binding energy is of the order of 20 meV. In small embedded layers this value may be increased because of reduced screening due to the image potential effects in presence of the SiO_2 layers.

Nevertheless, the rough agreement between PL findings and the results for the DBM and BOM in position and progression of the size-dependent energy gaps leads to the conclusion that in the fabricated MQW structures one has predominantly one-dimensional confinement (though with deviations from rectangular potential wells) and that the interfaces are almost hydrogen-free. To check the latter point, Fourier-transformed infrared spectroscopy (FTIR) was performed on the Si/SiO_2 quantum well samples. In accordance with previous studies on RPECVD-grown SiO_2 layers,[29,30] no IR absorption originating from the hydroxyl-related Si-OH bonds at 3650 cm^{-1} (Ref. 31) nor the hydrogen-related Si-H bond at 2100 cm^{-1} (Ref. 31) could be observed in the measured FTIR spectra. This result supports the picture of an almost hydrogen-free Si/SiO_2 interface in the structures investigated.

However, the *ab initio* results for the introduction of hydrogen bonds at the Si/SiO_2 interface suggest a significant increase in the effective band gap. Thus, the idea of incorporation of impurity atoms such as hydrogen which give rise to strong and highly polarizable bonds to Si atoms may be used to pave the way to a 1.8 eV band gap material leading to the highest achievable efficiency in tandem solar cells combining bulk Si wafers and quantum well structures.[4]

V. SUMMARY

In summary, we have analyzed the quantum confinement effect on the fundamental gap of Si/SiO_2 MQWs with nanometer-sized layers by comparison of *ab initio* band gap calculations and PL measurements. Taking into account complex interface geometries and effective many-body interactions, the comparison of theory and experiment shows that the Si/SiO_2 structures prepared by subsequent RTA are almost hydrogen-free and that their weak band gap variation is governed by an almost one-dimensional confinement. The hydrogen-free interfaces explain the sublinear thickness dependence found for the measured values. Interestingly, the theory predicts that the presence of hydrogen may enforce the confinement effect, at least for the electronic gap. However, also other special interface preparations may contribute to an enhancement of the confinement effects. Si-O-Si bridge bonds in the interface tend to give rise to higher gaps than, e.g., Si=O dangling-bond reconstructions.

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