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ScienceDirect

Surface Science 601 (2007) 2223–2231

SURFACE SCIENCE

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First nucleation steps during deposition of SiO_2 thin films by plasma enhanced chemical vapour deposition

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Received 29 December 2006; accepted for publication 19 March 2007
Available online 24 March 2007

Abstract

The initial nucleation stages during deposition of SiO_2 by remote plasma enhanced chemical vapour deposition (PECVD) have been monitored by XPS inelastic peak shape analysis. Experiments have been carried out on two substrates, a flat ZrO_2 thin film and a silicon wafer with a native silicon oxide layer on its surface. For the two substrates it is found that PECVD SiO_2 grows in the form of islands. When the SiO_2 particles reach heights close to 10 nm they coalesce and cover completely the substrate surface. The particle formation mechanism has been confirmed by TEM observation of the particles grown on silicon substrates. The kinetic Monte Carlo simulation of the nucleation and growth of the SiO_2 particles has shown that formation of islands is favoured under PECVD conditions because the plasma species may reach the substrate surface according to off-perpendicular directions. The average energy of these species is the main parameter used to describe their angular distribution function, while the reactivity of the surface is another key parameter used in the simulations.

Keywords: Nucleation; Thin film growth; Plasma deposition; XPS; TEM; Background analysis; Monte Carlo simulation; SiO_2

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1. Introduction

Formation of the first nuclei during the growth of thin films constitutes a crucial step for the determination of their final microstructure and morphology [1]. Owing to this fact, the study of these first steps of growth has deserved a considerable attention from both experimental and theoretical points of view [2–5]. Most reports dealing with this subject concentrate on the description of nucleation for thin films prepared by evaporation (i.e. physical vapour deposition, PVD) and related methods [4–6] with, eventually, some consideration about the effect of the energy of other incoming particles when the thin film growth is assisted by ion bombardment (i.e. like in Ion Beam Assisted Deposition, IBAD, methods) [7]. In this context, only few works have been devoted to the study of the nucleation processes for thin films grown by plasma enhanced chemical vapour deposition (PECVD) procedures [8–10]. In particular, the initial stages of growth of SiO_2 thin films ($5 < d < 500$ A thickness) plasma deposited on polymer substrates were studied by Wertheimer et al. [9,10] by Rutherford back scattering (RBS). These authors found that the best description of the growth on this type of substrates was that of a layer by layer process.

From a mechanistic point of view, the situation is more complex by PECVD than by PVD. Thus, while in this latter case all the incoming particles are neutral and present a little dispersion of thermal energies, in the former neutral

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0039-6028/$ - see front matter © 2007 Published by Elsevier B.V.
doi:10.1016/j.susc.2007.03.027

and ion species with different kinetic energies may arrive to the surface. The present work aims primarily at developing an experimental approach based on X-ray photoemission spectroscopy (XPS) and transmission electron microscopy (TEM) for monitoring the initial nucleation steps of SiO_2 thin films prepared by PECVD. The selection of SiO_2 for the present study is justified because of the importance of thin films of this material for a large variety of processes and applications [11–13]. As a second objective, this work also tries to account for the effects on the nucleation mechanisms of some basic characteristic of the plasma processes that, from previous work, we know that may control the final morphology of the films [14]. In particular, we simulate the possibility that plasma species may attain the surface according to off-perpendicular directions. In addition, we assume that the magnitude of the interaction between these species and the surface can vary depending on the plasma characteristics.

The description by XPS of the nucleation and particle growth during the initial steps of formation of the films is based on the analysis of the shape of the background behind selected photoemission peaks of the substrate and the deposited SiO_2 after successive deposition steps. The method relies on the Tougaard's concepts of inelastic scattering or electrons in solids [15,16]. In addition, transmission electron microscopy (TEM) analysis was used to confirm the type of growth mechanism when silicon wafers were used as substrates. The theoretical description of the growth process was carried out by means of a kinetic Monte Carlo (KMC) model, where both the angle of the trajectories of the plasma species incoming to the surface and the energy of interaction between these species with the substrate surface can be varied [14]. A good description of the nuclei shape and size was possible by selecting appropriate parameters for the energy and trajectory of the plasma species.

2. Experimental

The substrates used for the SiO_2 deposition were a piece of a Si(100) low p-doped wafer and a very compact and flat ZrO_2 thin film prepared by Ion Beam Induced Chemical Vapour deposition (IBICVD) [17]. The choice of this material is justified because it has been proposed as a potential candidate for high-k dielectric in microelectronic [18]. Prior to the deposition of SiO_2, the silicon wafer and the ZrO_2 thin film substrates were exposed to the plasma of oxygen to saturate its surface with oxygen. The substrates were located in the preparation chamber of a XPS spectrometer where all the deposition experiments were carried out. After each SiO_2 deposition step, the samples were transferred to the XPS main chamber for its analysis by XPS in a VG-ESCALAB 210 spectrometer.

PECVD deposition was done in the preparation chamber of the XPS spectrometer. The plasma source consisted of a quartz tube of 15 mm diameter fitted to the chamber. The gas mixture, consisting of argon and oxygen (1:1), was ignited by means of a resonant cavity powered by a commercial microwave generator (2.45 GHz). An excitation power of 75 W was used for all experiments. Dimethylsilane $(CH_3)_2SiH_2$ (DMS) was used as precursor for all experiments. Vapour of the precursor was dosed directly onto the surface of the substrate by means of a stainless steel tube and a valve connecting the precursor bottle to the chamber. While dosing the precursor onto the surface, the substrate was exposed to the plasma according to a remote configuration. The partial pressure of the precursor during deposition was 1×10^{-4} mbar for a total pressure (i.e. $O_2 + Ar + DMS$) of 1.6×10^{-1} mbar due to all plasma gases. These conditions render rather low deposition rates that permit the XPS analysis of the initial stages of growth of SiO_2 onto the two substrates. Prior to the deposition experiments of SiO_2 the substrates were exposed to the plasma of oxygen to saturate its surface with oxygen. Native silicon oxide thickness of 13.2 Å was estimated for both XPS peak shape analysis and direct TEM observation.

XPS spectra were recorded by using the unmonochromatised Mg Kα radiation as excitation source and by setting the electron energy analyzer in the constant pass energy mode at a value of 20 eV. The Si KLL Auger spectra were recorded by using the electron Bremsstrahlung radiation of the same source. General spectra in a binding energy (BE) region from −200 to 1100 eV were recorded. Selected regions of these spectra were used for the peak shape analysis [19]. In addition, zone spectra with better resolution were recorded for the different peaks to get more precise chemical and/or electronic information of the layer.

The XPS inelastic peak shape analysis consists of the study of both the peak intensity and the peak shape in a region 50–100 eV behind the elastic photoemission or Auger peaks. We used the QUASES [20] software to model and reproduce the experimental spectra. The basis of the method relies on the Tougaard's concepts of inelastic background analysis derived from an appropriate description of the electron energy losses during transport in the solid [15,16]. Outputs from the calculations are an in-depth concentration profile of photo-emitting atoms and/or the resulting surface morphology of the existing aggregates on the surface. The equations implemented in the software permit to simulate the background shape in a wide energy range below the elastic peak by choosing morphology factors such as c, the surface coverage, and h, the average island or layer height. For all cases studied here, a homogeneous distribution of orthorhombic islands of SiO_2 was efficient to reproduce the shape of the experimental spectra. Consequently, it was possible to determine, for each deposition stage, the average height of the deposited particles and the surface fraction of covered substrate. The following photoemission peaks were considered for the XPS inelastic peak shape analysis:

- SiO_2 on the silicon wafer substrate: O1 s and OKVV peaks of native and deposited SiO_2.

- SiO_2 on the flat ZrO_2 thin film substrate: Zr3p peak of the substrate and Si KLL peak of the deposited SiO_2.

The QUASES analysis was performed according to the following steps: (i) removal of backgrounds from the experimental spectra; (ii) simulation of backgrounds under the assumption of a given distribution of particle sizes; (iii) comparison of experimental and calculated spectra.

TEM analysis of the deposited SiO_2 particles was done with special specimen prepared simultaneously to those used for XPS background analysis. Silicon discs of 3 mm diameter were used for this investigation. They were cut out from one single crystalline silicon wafer piece. Cutting was done with an ultrasonic preparation machine, under a flow of water and silicon powder solution. The specimen substrate was thinned in the centre by argon ion bombardment up to make a hole. In the regions close to the hole the substrate was so thin that it was nearly transparent to the accelerated electrons of the TEM microscope. A homemade specimen holder was used to manipulate and to introduce these substrates in the XPS preparation chamber for the deposition experiments. In addition to this TEM normal view analysis used to visualize the deposited silicon dioxide particles, cross section images were taken by TEM. In this case preparations were made from silicon substrates after the deposition of SiO_2 and with substrates not subjected to any thinning process. The specimen was cut with a diamond cutter pen into thin stripes of about 3 mm length and 1.5 mm width. The stripes were glued face to face with a duraplasty adhesive to form a sandwich and then were thinned by lateral ion etching.

3. Kinetic Monte Carlo simulation method

KMC simulations have been previously used in the literature for the simulation of different growth processes, such as epitaxial growth [21] or PECVD [22]. A detailed description of these MC simulations can be found elsewhere [23,24]. In our KMC model we have incorporated some distinct features to account for the high reactivity of the silicon oxide species produced by PECVD and the high binding energy of the SiO_2. This means that the solid-on-solid approximation, usually considered in the modelling of the epitaxial growth of metallic films [25], is not taken into account. As a result, the imposition of some restrictions to surface diffusion of species, justified because of their high binding energies to the surface, will favour the development of microporosity in the films. In addition, we assume the possibility that the velocities of the particles arriving to the surface present a certain distribution function. In particular, following the work of Karabacak et al. [26], we assume that the incoming particles follow a Maxwellian energy distribution function. This possibility is a characteristic feature of the PECVD processes and according to a previous work [14] is the reason why the plasma species may arrive to the surface according to off-perpendicular. It is important to note that this assumption is congruent with the physical characteristics of a plasma, but probably not applicable to "line of sight" techniques like physical vapour deposition or molecular beam epitaxy where the incoming particles follow straight trajectories.

According to our previous work [14], the probability for a particle to reach the surface with an angle θ smaller than Θ with respect to the normal direction of the surface is

$$P[\theta < \Theta] = 1 - \cos\Theta \frac{\exp(z^2\cos^2\Theta)[1 + \mathrm{erf}(z\cos\Theta)]}{\exp(z^2)[1 + \mathrm{erf}(z)]}$$

with z being a normalized velocity given by:

$$z^2 = \frac{Mv_0^2}{2k_\mathrm{B}T}$$

where v_0 is an average directed velocity of the particles towards the surface, M means their average mass and k_B and T are the Boltzman constant and the temperature of the particles expressed in Kelvins.

Therefore, depending on the value of the normalised velocity z we can simulate situations ranging from nearly vertical incidence of the particles to a pure Maxwellian energy distribution of the incoming particles with a large span of angles of incidence. In the limit of pure vertical incidence the previous expression has the form of a Heaviside step function $H(\Theta)$.

The growth process is modelled as follows: particles arrive to the surface with a certain angular distribution function $f(\theta)$, so that $f(\theta)\mathrm{d}\theta$ is the probability for a particle to reach the surface with an angle comprised between θ and $\theta + \mathrm{d}\theta$ with respect to the normal direction of the surface. This can be obtained from the derivative of the previous expression or approximated as a Dirac's delta, that is, $f(\theta) = \delta(\theta)$, for a pure normal incidence.

Once the plasma species reach the surface, they get physisorbed (i.e. they constitute some kind of ad-species) and are allowed to diffuse along the surface until either chemisorption or desorption takes place. Note that this physisorption occurs at the first contact with the surface, so that the usual solid-on-solid approximation [25] is not considered in this model. This means that our model allows for the presence of a variable porosity of the samples, in agreement with the experimental results obtained for oxides grown by PECVD that present densities which are normally 10% or even smaller than that of the bulk material [27]. The presence of such physisorbed state is supported by the current knowledge about surface interactions of Si-based precursors during CVD and PECVD [28].

The chemisorption is controlled by the presence at the surface of dangling bonds, whose density is determined by a certain parameter p_0, defined as the probability of having a dangling bond at each terminal position of the surface. This parameter is therefore a measure of the reactivity of the surface: $p_0 = 1$ means a dangling-bond saturated surface, while $p_0 = 0$ is a chemically inert surface. The final area that ad-species are allowed to explore before desorption will depend on both this parameter and on the energy of the physisorbed state. This latter, in the absence of reactive chemisorption sites, will control the characteristic diffusion length of the ad-species before desorption. Adjustment of this parameter during the simulations would also provide a way to distinguish between the different chemical nature of the growing film and the substrate.

Another kind of processes considered in the model is the existence of surface relaxation leading to cross-linking interactions in the film. During film growth, chemisorbed particles can rearrange themselves trying to maximise the number of nearest neighbours. This process contributes to the results obtained, a decrease of the porosity of the films. In the growth of oxides, diffusion of chemisorbed species is hindered by the characteristic high bonding energies of these materials. Therefore, in this model we have considered the relaxation of only single bonded chemisorbed particles. These particles are allowed to relax to neighbouring places, so that rocking and folding of these terminal surface species can be described.

In this work we have focused on the study of the early stages of growth of SiO_2 thin films deposited onto an oxide substrate (i.e. SiO_2 or ZrO_2), so that the interaction of the particles with either the film particles or the clean surface of the substrate is of similar nature. According to the results obtained, a certain surface reactivity (modelled with increasing values of p_0) and the arrival of incident particles following an angular distribution function are the two main factors which control the appearance of nanometer-sized islands during the first stages of growth. Within this scheme the growth of the SiO_2 particles onto an oxide other than silicon oxide can be modelled by assuming different degrees of interaction with the substrate through the assumption of different values of the parameter p_0.

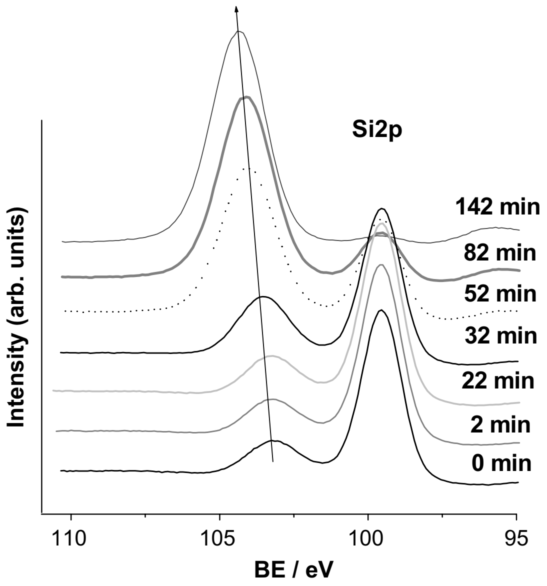

Fig. 1. Si 2p photoemission spectra corresponding to the deposition for the indicated periods of time of SiO_2 on a silicon substrate covered with a native compact layer of 13.2 A thickness of the same oxide. The spectra are displaced vertically for clarity in the observation.

4. Results and discussion

4.1. Deposition of SiO_2 by PECVD

Fig. 1 shows a series of Si 2p photoemission peaks corresponding to successive plasma deposition of SiO_2 for increasing periods of time. It is apparent in this figure that after each deposition step the intensity of the Si 2p peak at ~100 eV BE due to Si^0 [29] progressively decreases while the intensity of the peak at a BE equal or higher than 103 eV due to Si^{4+} species increases. A similar effect can be observed when looking at the Si KLL Auger spectra (data not shown). These results indicate that SiO_2 is being deposited on the surface of the silicon substrate. A parallel increase in the O1 s and OKVV intensities (Fig. 2) confirms this evolution. It is interesting in the spectra of Fig. 1 that the Si 2p peak due to Si^{4+} species progressively changes its energy position as the amount of deposited SiO_2 increases. An equivalent effect was observed when looking in detail at the O1 s and O KVV peaks in Fig. 2. This shift can be attributed to the accumulation of charge at the interface between the silicon substrate and the SiO_2 overlayer, a well know effect in interfaces involving insulating materials [30,31].

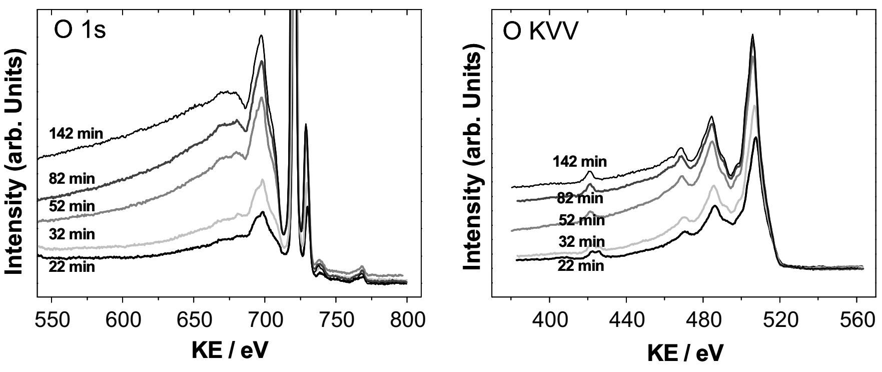

Fig. 2. Selected O1 s and OKVV wide scan spectra used for peak shape analysis. The horizontal scale refers to the kinetic energy of the electrons. The spectra are displaced vertically for clarity in the observation.

4.2. XPS inelastic peak shape analysis for the first nucleation stages of SiO_2 deposited on Si

Inelastic peak shape analysis of the Si 2p and Si KLL spectra would be very complex because these peaks are the result of the contribution of two different chemical species, one due to the substrate (i.e. Si^0 species at ~99.5 eV) and the other to the layer (i.e. Si^{4+} species with a variable position between 103.1 and 104.3 eV). Therefore, peak shape analysis has been carried out with the O1 s and O KVV spectra which are due to a single peak attributed to oxide ions, mainly of the deposited SiO_2. Fig. 2 shows the O1 s and O KVV lines for successive deposition steps of SiO_2 on Si. Similar spectra were recorded on ZrO_2. It can be observed that the background height behind the main peaks increases as the amount of deposited SiO_2 increases. Simulation of these spectra with the QUASES code provides a description of the SiO_2 thin film growth during the initial periods of deposition [32]. It is important to comment here that the bare Si substrate is already covered by a ~13 Å thin native oxide layer as determined by QUASES calculation and confirmed by TEM analysis (see next section). The existence of this layer was explicitly considered in the simulation with QUASES as discussed next. This means that for the reproduction of the background of the spectra both the effect of this layer plus that of the deposited SiO_2 was taken into account.

4.3. Simulation of SiO_2 deposition with QUASES

The best simulations carried out with the spectra in Fig. 2, for which the calculated spectra fit completely the background of the experimental spectra, are obtained by assuming that the SiO_2 grows in the form of particles whose size increases for successive deposition experiments. Note that other options like for example monolayer growth were excluded by the criteria used for fitting. The results of the simulation under the assumption of particle formation are reported in Fig. 3 where the average height of the islands (h) is plotted against the surface coverage (c) for a series of experimental situations. Only four cases have been considered for a surface coverage around 0.6 and higher. The value 1 in surface coverage relates to a full covered surface of the substrate. The used spectra correspond to depositions times from 32 to 142 min, where accuracy of the analysis is assured by the intensity of the contribution of the oxygen associated to the deposited SiO_2. For a coverage lower than 0.6, the intrinsic inaccuracies of the simulation, particularly in the present case where the oxygen peaks are due to both the native SiO_2 of the substrate and the deposited SiO_2 overlayer, restrict the reliability of the calculations. As a reference for the analysis of bulk SiO_2, the spectrum of the sample after deposition for 142 min (i.e. see the corresponding spectrum in Fig. 2) was used. To assess the equivalent layer thickness (EHT) that was deposited in each case, Fig. 3 includes a series of dashed curves which are calculated according to $c \times h = \text{EHT}$. Thus, EHT represents the curves for a thickness of deposited material equivalent to that of a homogeneous and continues overlayer of the thickness specified in the plot (upper X-axis). In Fig. 3 two types of simulations are reported, one based on the O1 s spectra and the other in the OKVV spectra. They show some discrepancy for coverages between 0.6 and 0.8, but coincide rather well for higher c values. This type of discrepancies may appear in this type of QUASES calculations and is due to the difficulties of the analysis in a complex system like the one considered here. A good approximation would be to consider that the discrepancy defines the error bar of the analysis and that the real situation is an intermediate curve comprised between the two plotted lines.

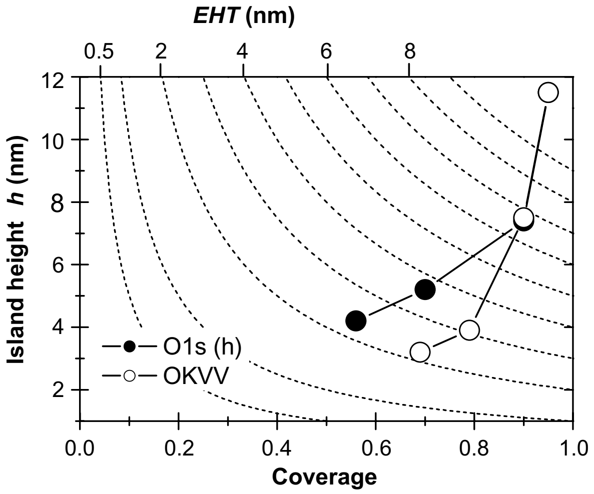

Fig. 3. Plot of island heights against surface coverage for SiO_2 deposited by PECVD on a silicon substrate for increasing periods of time from 32 to 142 min. Two set of data points are reported depending on whether the analysis has been performed with the O1 s or the OKVV peaks. The dashed lines represent amounts of substances (EHT), as indicated (see text).

The results in Fig. 3 indicate that the SiO_2 particles deposited by PECVD on the surface of the silicon substrate grow in the form of separated nanoparticles that eventually coalesce when they grow in size (i.e. a Volmer–Weber type of growth [33]).

A similar growth mode was obtained for the experiment conducted on the flat surface of ZrO_2. The results for this SiO_2/ZrO_2 system are shown in Fig. 4. It is important to comment that the chosen spectra correspond to the same experiments selected in the case of the SiO_2/Si system (i.e. the deposition was carried out simultaneously on the two substrates for the same periods of time). It is apparent in this graph that SiO_2 also grows in the form of islands on the surface of ZrO_2. However, although the differences are small, these islands coalesce and cover completely the surface when they have reached heights slightly lower than in the case of the silicon wafer substrate. On polymer substrates, Wertheimer et al. [9,10] found that plasma deposited SiO_2 grows according to a layer by layer mechanism, a feature that was attributed to that polymer surfaces were

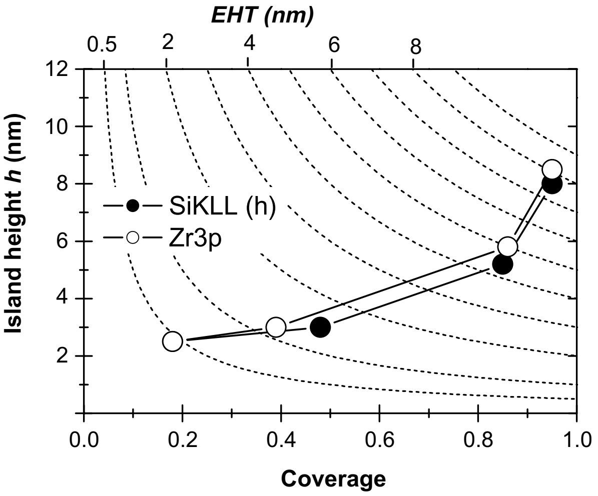

Fig. 4. Plot of island heights against surface coverage for SiO_2 deposited by PECVD on a ZrO_2 flat thin film for increasing periods of time from 32 to 142 min. Two set of data points are reported depending on whether the analysis has been performed with the Zr 3p or the Si KLL peaks. The dashed lines represent fixed EHT, as indicated (see text).

rendered "wettable" during the first moments of exposure to active oxygen of the plasma.

4.4. TEM characterization of deposited SiO_2 particles

The peak shape analysis based on Tougaard's method gives an average assessment on particle morphologies and sizes. To prove the reliability of this analysis at a microscopic scale, we have intended the direct observation by TEM of the particles formed by the PECVD deposition of SiO_2 on the silicon substrate (a similar analysis would not be possible on ZrO_2, a material with a much higher electron cross section than silicon that, therefore, would absorb most electrons used for observation and would not permit the TEM detection of the SiO_2 particles). Fig. 5 shows two planar TEM micrographs taken for the clean Si substrate and after one hour SiO_2 deposition. This image shows the formation of SiO_2 particles with a size ranging between 3 and 8 nm, in good agreement with the results obtained from the Tougaard's analysis of the XPS spectra. The electron diffraction pattern reported in Fig. 5 shows that besides the points due to the single crystalline Si substrate, there are a series of diffuse rings at distances characteristic of SiO_2. This result points to that particles present some crystallinity, even if they were formed at room temperature. However, it is not quite clear at the present stage whether this partial crystallization has occurred as an effect of the electron irradiation during TEM observation or if it is an intrinsic characteristic of the SiO_2 particles prepared by PECVD in this experiment. This first assessment of particle size and morphology is confirmed by the TEM cross section images in Fig. 6. It has to be noted that the thickness of the granular SiO_2 layer depicted in this latter figure is the result of the microscope observation at an angle slightly tilted with respect to the cross-section normal (i.e. the image reflects the accumulation of particles at different planes below the first surface exposed to the electron beam).

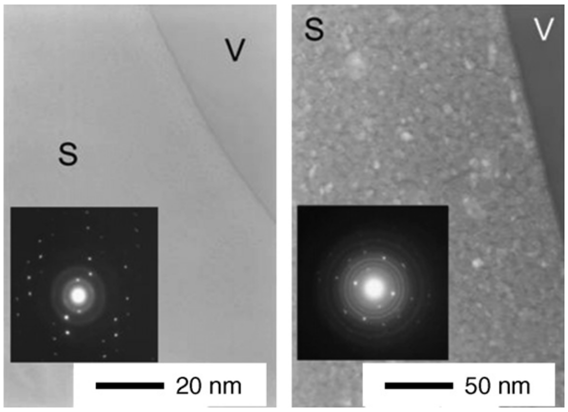

Fig. 5. Normal TEM micrographs of a thinned silicon wafer without (left) and with (right) SiO_2 particles deposited on its surface for 1 h. The figure also includes the electron diffraction diagram for the two samples. S and V refer to "substrate" and "vacuum" regions.

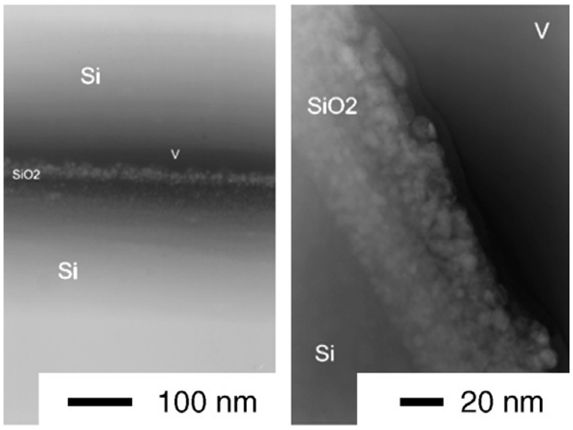

Fig. 6. High resolution TEM cross section images of the SiO_2 film deposited on the Si substrate. Left and right images correspond to low and high magnifications.

4.5. Monte Carlo simulation of the PECVD formation of SiO_2 nanoparticles

In Fig. 7, 80 × 80 nm images of simulated films of 6 nm nominal thickness are presented for a Maxwellian energy distribution function of incident particles (i.e. $z = 0$) and different surfaces reactivities parameterized by assuming values of $p_0 = 0.05$ (Fig. 7a), $p_0 = 0.01$ (Fig. 7b) and $p_0 = 0.005$ (Fig. 7c). Also, in Fig. 7d an image is presented for the same surface conditions than those of Fig. 7b, but considering the vertical incidence of the incoming particles. Looking at the simulations, it is found that islands appear when a Maxwellian energy distribution function is assumed

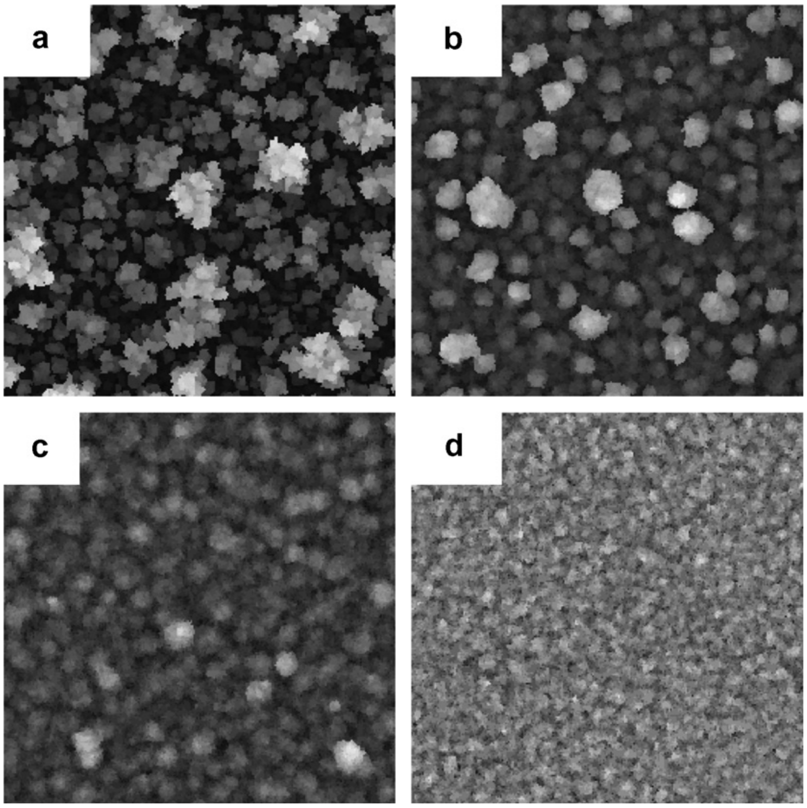

Fig. 7. (a–c) Simulated thin film topographies for a Maxwellian energy distribution function of incident species and different surface reactivities modelled through parameter values of $p_0 = 0.05$ (a), $p_0 = 0.01$ (b) and $p_0 = 0.005$ (c). The image (d) has been obtained with $p_0 = 0.01$ and a vertical incidence of incoming particles.

and the surface reactivity is relatively high (i.e. for relatively high p_0 values). In fact, from the comparison of Fig. 7b and d it is clear that formation of big islands is favoured for an off-perpendicular incidence of the incoming particles, a feature that can be considered typical of PECVD processes [14]. On the other hand, the small differences observed by XPS for the experiments on the ZrO_2 and the silicon substrates (cf. Figs. 3 and 4) could be accounted for by a slightly different reactivity of these two substrates towards the plasma species (i.e. slight differences in the p_0 parameters at the beginning of the deposition when the plasma species interact directly with the substrate).

It is important to mention that the island formation under our growth conditions was a non-equilibrium process, that is, during the film growth the surface never reached the thermodynamical equilibrium. This is due to the fact that the characteristic time for a relaxation process in the SiO_2 thin film ($\tau \sim 1$–10 s for an energy barrier of around 0.5 eV at room temperature) is not much higher than the assumed characteristic time between the adsorption of different particles ($t \sim 1$ s for a growth rate of 1 Å/min). Therefore, the number of relaxation processes per incoming particle is not high enough to let the system relax to thermodynamical equilibrium. For a higher number of relaxations or cross-linking processes (for instance by reducing the growth rate or increasing the substrate temperature) the evolution of the system would come closer to a typical equilibrium behaviour.

It is also interesting to compare the different line profiles of the simulated surfaces. In Fig. 8 selected line profiles are presented for simulated surfaces obtained using the same parameters than in Fig. 7 as a function of the amount of deposited material (i.e. equivalent to the deposition time in a real experiment). For a Maxwellian energy distribution function of incident particles (i.e. Fig. 8a–c) the growing surface is mainly formed by islands with a characteristic size of some nanometers that increases with the film thickness. For a given thickness, the height of such islands is greater the higher is the surface reactivity (i.e. high p_0 values). According to the simulation, the coalescence of the islands and therefore the total coverage of the substrate takes place for an island height ranging from 2 to 10 nm depending on the parameters used for simulation. Thus, it is worthy of note in Fig. 8a that big particles up to around 10 nm height are formed before that the substrate is completely covered by SiO_2. This situation approaches the experimental situation described by the points at high coverages in Figs. 3 and 4. It must be also mentioned that, as deduced from the KMC simulations and found experimentally, particles coalescence must prevent the formation of columnar structures in the thin films. These columnar structures are typical for PVD processes [34] but are not experimentally observed for thin films of SiO_2 grown under

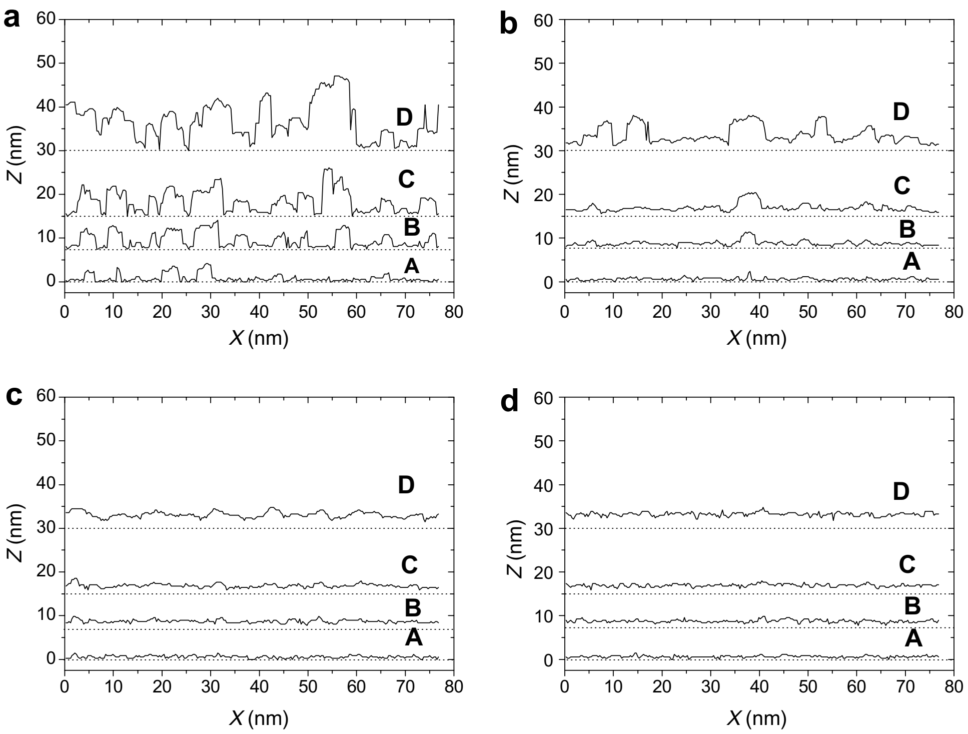

Fig. 8. Line profiles taken from the simulated PECVD growth for the same conditions (a–d) than those used in Fig. 7. The A–D lines in each plot, displaced vertically for clarity, correspond to the deposition of increasing amounts of material (i.e. simulation of the deposition for increasing periods of time). Dotted lines correspond to the displaced zero position where no deposition has taken place.

experimental conditions similar to those used in the present work [35]. The presence of lateral growth, enhanced in the simulations by disregarding the solid-on-solid approximation, is of paramount importance in order to prevent the appearance of such columnar structures.

From the profiles in Fig. 8 it is also apparent that there are two distinct regions in the simulated films: the islands are characterised by heights of the order of several nanometers, while the regions between them have a thickness ranging typically between 0 (i.e. free surface) to 2 nm. As shown in Fig. 8, the island coverage increases with film thickness until coalescence takes place. Depending on the conditions, a coverage of up to 90% would be expected only for a film thickness of 15 nm (e.g. Fig. 8a–d). These results are in clear agreement with the XPS and TEM experimental results presented in the previous section.

One of the limitations of the model presented in this work is that the simulation is performed in a cubic lattice. This approach, although it is rather common for simulating Si-based materials [22,36], has an important drawback: the number of nearest neighbours of each particle in the lattice is six, while in SiO_2 the Si is 4-coordinated with a tetrahedral symmetry. The use of a 4-coordinated diamond lattice as well as the simulation of the attenuation of the photoemission signal from the substrate in the XPS experiment are two open issues that should be addressed for an even better convergence between experimental and simulated results.

5. Conclusions

The comparison of the results by XPS about particle formation with the direct assessment by TEM of particle sizes has shown that XPS inelastic peak shape analysis of photoemission spectra can be a useful experimental tool to characterize the initial stages of nuclei formation of thin films.

The results obtained for the first nucleation steps of SiO_2 thin films deposited by PECVD have shown that they consist of the formation of particles that grow in height up to coalescence when they have a sufficiently big size. This behaviour occurs on both a Si wafer and a ZrO_2 flat substrate consisting of a thin film of this material. This result contrasts with earlier studies by Wertheimer et al. [9,10] showing that the SiO_2 grows in a layer by layer way on polymer substrates. In comparison with other growth processes described in the literature for other materials and methods [1–5], a characteristic feature of the PECVD growth of SiO_2 on our two substrates is that the size of the particles before coalescence can be very high. To account for this experimental evidence we have performed a series of KMC simulations for several average energies of the plasma species and reactivities of the growing surfaces. This study has shown that important clues to account for the PECVD growth of SiO_2 in the form of big particles are the existence of a high surface reactivity and the arrival of plasma-species to the surface from off-normal directions.

In PECVD processes the energy of the plasma species can be easily changed by modifying plasma parameters like gas composition, power, application of electrostatic and/or magnetic fields, etc. For example, it is to expected that changing the bias voltage applied to the substrate may significantly modify the energy of the plasma species and, therefore, the mechanism of growth. Taking this into account, our results and their modelling by KMC simulations indicate that the morphology of thin films prepared by PECVD would be easily modified by just changing this kind of plasma parameters.

Acknowledgements

We thank the Spanish Ministry of Science and Education for financial support (Grant No. MAT 2004-01558). One of us (D.D.) thanks the German Academic Exchange Service (DAAD) for a grant to carry out this work at the ICMSE.

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