Nucleation of strontium titanate films grown by PLD on silicon: a kinetic model

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Abstract

Nucleation and growth of strontium titanate (SrTiO$_3$) films, prepared by pulsed laser ablation deposition, has been investigated during on a (100) silicon substrate surface, using atomic force microscopy. A nucleation kinetic model has been derived from an analysis of the particle size distribution. The reconstructed nucleation trend was characterised by a systematic behaviour: the nucleation rate, negligible at the beginning, reaching a maximum after a certain time and tending to zero for longer deposition time. This behaviour prompted the design of a simple model which correlates these phenomena to two specific aspects: i) the nucleation occurs at certain limited number of sites on the substrate surface; ii) the nucleation process shows a temperature-dependent incubation time. In this model, the incubation time is related to the formation time of a 'critical SrTiO$_3$ cluster'. The size of the critical cluster is determined both by thermodynamic quantities and by the amount of interface misfit strain energy of SrTiO$_3$ lattice with respect to substrate. © 1997 Elsevier Science S.A.

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1. Introduction

Long-range Coulomb interactions between charged elements of a crystal are important forces during film growth of ionic materials. By the hard task of developing a complete microscopic model for growth of complicated ionic materials such as complex oxides, it is interesting to first examine empirically how film growth proceeds. A particular example is the class of layered strontium titanate on silicon, known as Metal-Insulator. The SrTiO$_3$ (STO) thin films [1] are used for numerous electric applications in very large scale integrated (VLSI) circuits such as dynamic random access memories (DRAMs) [2] and antireflective coating in optoelectronics devices. In addition, STO films could be used as very fast oxygen sensors since their electrical conductivity changes fast with the ambient oxygen partial pressure [3].

Pulsed laser ablation deposition (PLD) seems to be the best technique to obtain epitaxial as-deposited films at relatively low temperatures and STO has been already used as a buffer layer on silicon and on sapphire [4,5], but a wide study of the deposition of STO on Si by PLD has not yet been realised.

In this work, a nucleation study of the strontium titanate films using atomic force microscopy (AFM) has been carried out. The STO deposition on heterogeneous substrates such as Si is quite a complex process mainly because of the contemporary contribution of different elements at the Si/SrTiO$_3$ interface, which are difficult to disentangle. Among them we need to consider: i) the nucleation activation by solid substrate surface, and ii) the effects of simultaneous reactions at the substrate surface. However, the experimental data observed can be described by a simple kinetic model, that relies mainly on two physical phenomena: i) a limited number of active sites for nucleation and ii) an incubation time related to the formation of critical clusters. The method used to observe the SrTiO$_3$ nucleation kinetics and a proposed growth model are presented.

2. Experimental

The pulsed laser ablation deposition was carried out using a 308-nm XeCl Lambda excimer laser. The beam
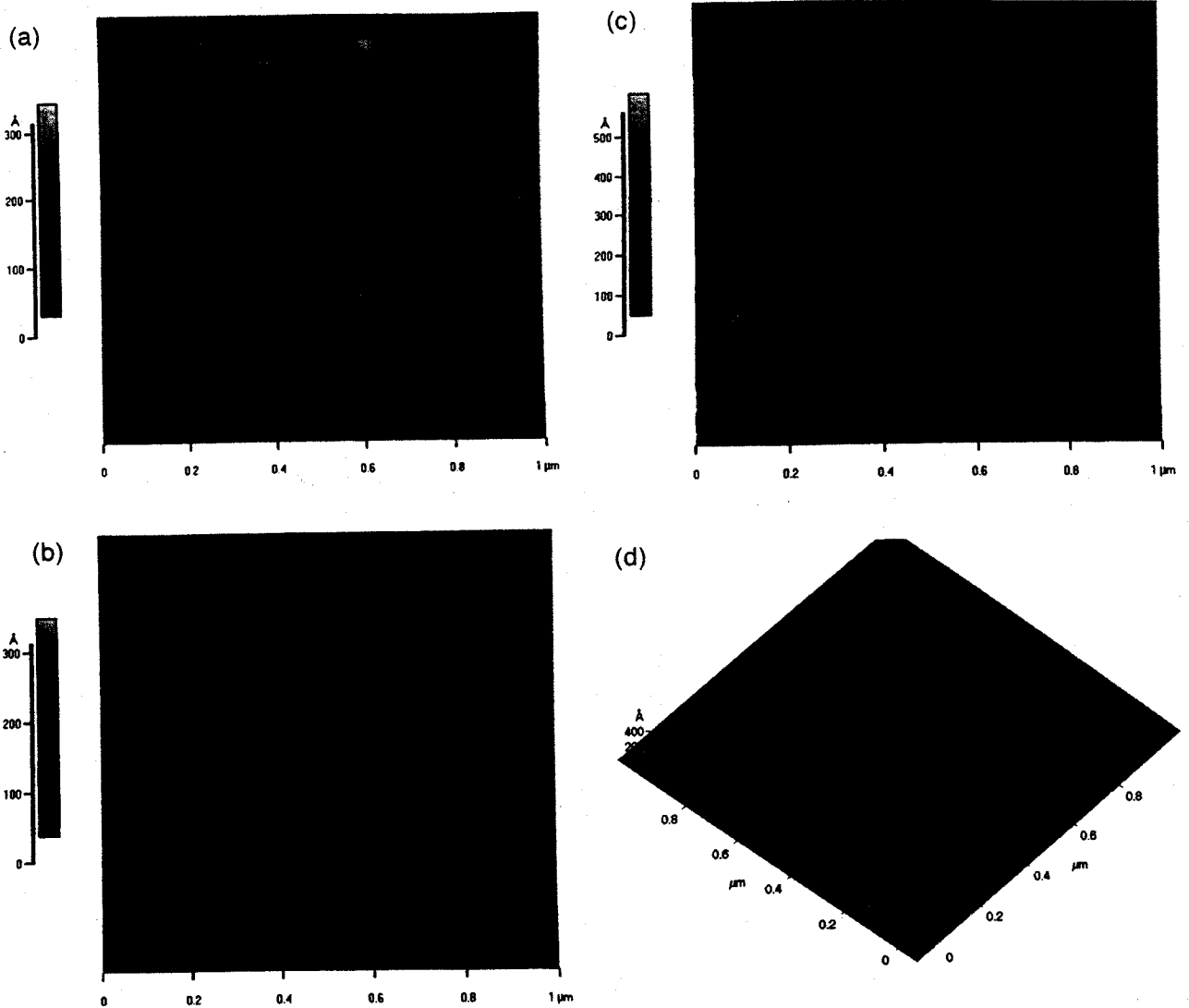
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Fig. 1. AFM micrographs of the SrTiO₃ thin film for the STO1, STO2 and STO3 samples, respectively: (a–c) two-dimensional projection scanned over area of 1 × 1 μm², (d) three-dimensional image of the STO1 sample scanned over an area of 1 × 1 μm².

was focused onto the ceramic source target to an energy density of 3.6 J/cm² and a pulse width of 17 ns and a pulse repetition rate of 10 Hz were used for the growth experiments. High density SrTiO₃ targets were obtained by sintering ball milling SrCO₃ and TiO₂, calcining at 900°C and sintering the pressed discs at 1350°C. The substrates were 10 × 10 mm squares cut from a (100) silicon wafer which were mounted onto the heater block at a distance of 35 mm from the target. The sample and furnace temperature was measured using a thermocouple behind the substrate. Films were deposited under oxygen pressure of 200 mTorr at 550, 600 and 800°C, corresponding to samples STO1, STO2 and STO3, respectively. At the end of the ablation, the chamber was maintained at this pressure regime and the films were allowed to cool at the normal rate. The nominal film thickness was ≈ 1000 Å.

The microstructure, grain size and surface topography of the crystallised films were measured by atomic force microscopy, using an STM/AFM autoprobe (CP Park Scientific Instruments), with high resolution scanner with a maximum range of 5 × 5 μm². Contact mode atomic force images of the as-deposited film are shown in Fig. 1a–c for the different deposition temperatures. A three-dimensional AFM image of sample STO1, with a peak–valley ratio (R_{p-v}) of about 200 nm is shown in Fig. 1d. Although there are submicron-sized droplets on the surface, the films have a regular smooth surface and a dense structure.

3. Growth model and discussion

The nucleation rate as a function of time on a single sample can be determined if the single particle growth rate and the particle size distribution are known. Assuming that a grain of radius (r), which is present on a surface after a deposition time (t_g), derives from a nucleus which has

formed at a previous time t_b, this time can be determined from the radius r and the deposition time t_g when the single particle growth law is known. By defining a distribution function $F(r,t_g)$ such that:

$$F(r,t_g)dr \tag{1}$$

is equal at the number $dN(t_g)$ of nuclei which have formed in the previous time interval (t_b) in an interval of time dt_b corresponding to dr; hence:

$$-F(r,t_g)\partial r(t_g,t_b)/\partial t_b = \partial N(t_g,t_b)/\partial t_b \tag{2}$$

The distribution function $F(r,t_g)$ can be obtained directly from the AFM image counting the number of particles (considered to be spherical) associated at each particle size r.

For the simple case of isotropic growth with constant nucleation and growth rates (α), each particle is considered to be a sphere with the radius αt [6], and the growth, occurring in the thin film formation, may be approximated by a time dependence of the type:

$$r(t) \cong \alpha t^n, \tag{3}$$

where α is a function of the temperature, n is an exponent related to growth mechanism, and $t = t_g - t_b$; assuming no surface diffusion on the substrate and that growth is possible only at certain nucleation sites [6].

Since its formation, the size of the nucleus is considered to be negligible with respect to the smallest measurable particle size present at the time t_g, i.e., the time when the observation is made. For a $SrTiO_3$ film growing on a
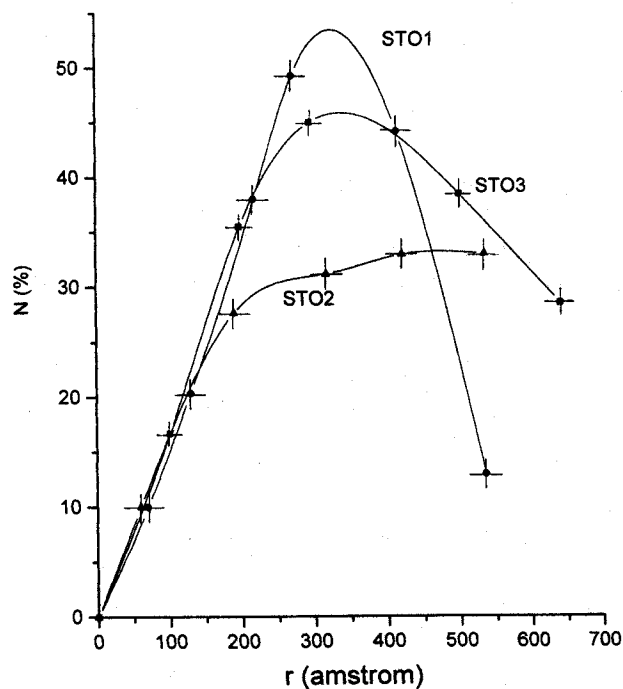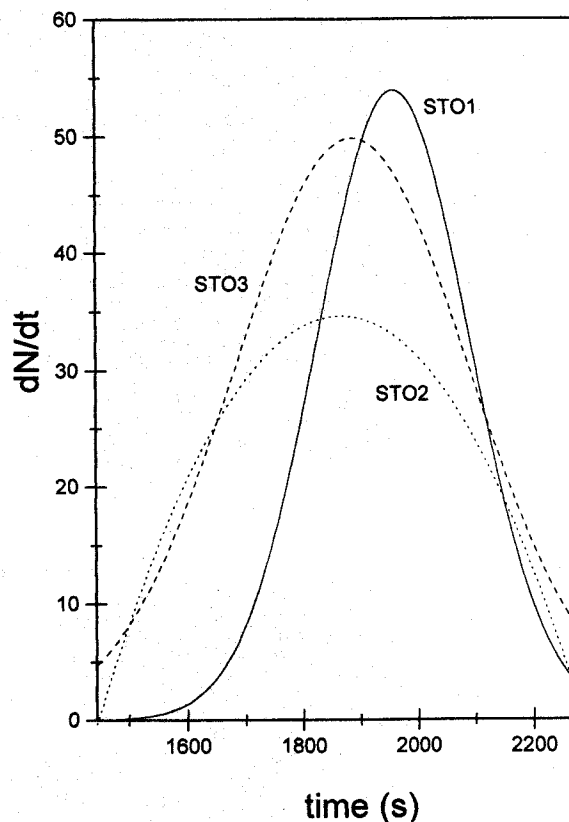

Fig. 3. Nucleation rate derived from Eq. (5) as a function of the time at temperatures of 550, 600 and 800°C, corresponding to the samples STO1, STO2 and STO3, respectively.

silicon substrate, the experimental data obtained suggest that a linear approximation may be a reasonable first guess, i.e., that the volume growth rate is proportional to its surface area, thus:

$$r = \alpha t, \text{ then } dr/dt_b = dr(t_g,t_b)/dt_b = -\alpha \tag{4}$$

and by substituting in Eq. (2):

$$dN/dt_b = \alpha F(r,t_g), \tag{5}$$

where $r = \alpha(t_g - t_b)$ has been substituted in the function $F(r,t_g)$. This expression indicates that any functional dependence in r, shown by the particles size distribution, has a simple direct correspondence on the behaviour of the nucleation rate time dependence.

The particle size distributions observed for the three different temperatures are shown in Fig. 2, and the corresponding nucleation rates derived from Eq. (5) are plotted Fig. 3. The curves of Fig. 3 have been derived from the measurements obtained in Fig. 2. Firstly, the data for N vs. r, for each curve of Fig. 2 can fit into an equation of Gaussian form:

Fig. 2. Particle size distribution at temperatures of 550, 600 and 800°C, corresponding to the STO1, STO2 and STO3 samples, respectively.

$$y = A \exp\left[-2(x - x_c)^2/\omega^2\right]\Big/\omega\sqrt{\pi/2}, \tag{6}$$

where $y = N$, $x = r$; and: $A = 17851$, $x_c = 323.07$, and $\omega = 263.98$ (for the sample STO1); $A = 25293$, $x_c = 394.68$, and $\omega = 405.01$ (for sample STO3); a polynomial:

$$y = 0.884 + 0.163x - 1.97\,10^{-4}x^2 \text{ (for sample STO2)}.$$
(7)

After, r can be substituted by the relation $r = \alpha(t_g - t_b)$ using $t_g = 2280$ s and $\alpha = 1$ giving the curves shown in Fig. 3. A maximum is observed in the particle size distribution at a certain particle size. This maximum shifts toward higher sizes on increasing the deposition temperature. The estimated nucleation rate initially increases to a maximum and then falls for a long time.

3.1. Theoretical growth model

Assuming that the nucleation occurs on a certain finite number of sites, N_0 (present on the substrate surface or introduced there by a pre-treatment), where strained and possibly disordered clusters are kinetically favoured, bonds are formed at the interface between the SrTiO$_3$ atoms and the Si substrate and that a region extending to some interatomic bonds has a large contribution of strain energy due to the misfit between STO and silicon. Thus, two aspects, the finite number of nucleation sites N_0 and the presence of subcritical clusters, are assumed to be the main features at the basis of the nucleation kinetic model discussed in Section 3.1.1. The misfit strain energy contribution to the Gibbs condensation free energy together with the surface energy are considered to determine the subcritical cluster stability.

3.1.1. Influence of the finite number of nucleation 'site' on the nucleation kinetics

Let us first consider that the nucleation rate is proportional to the number of 'active sites', hence:

$$dN/dt = \beta[N_0 - N(t)],$$
(8)

where, N_0 is the number of 'active sites' present at the time $t = 0$, N_0 is considered to be temperature dependent, $N(t)$ is the number of nuclei formed after the deposition time t, and β is the steady state nucleation probability per unit time. For the moment, let β be a time independent constant. Integrating Eq. (8):

$$N(t_b) = N_0[1 - \exp(-\beta t_b)],$$
(9)

thus:

$$dN/dt_b = N_0\,\beta\exp(-\beta t_b)$$
(10)

Recalling Eqs. (8) and (10) and substituting in Eq. (5):

$$F(r) = A\exp(\beta r/\alpha) \quad \text{for } r/\alpha < t_g$$
$$F(r) = 0 \quad \text{for } r/\alpha > t_g$$
(11)

where:

$$A = (N_0/\alpha)\beta\exp(-\beta t_g)$$
(12)

and t_b was substituted by $r = \alpha(t_g - t_b)$.

The exponential time, decaying Eq. (10), provides an explanation for the decreasing nucleation rate at long times, associated with the progressive consumption of active nucleation sites. However, it fails to explain the initial short-time behaviour of the nucleation rate that has been observed to start from 0 and rise to a maximum. Consequently, it also fails to predict the presence of a maximum in the particle size distribution.

3.1.2. Complete time dependence of the nucleation rate

A more detailed model is needed to justify the short and long term behaviour of the nucleation rate. Thus, it is assumed that a distribution of atomic clusters grows on N_0 substrate sites at the start of deposition. The deposition starts STO atoms as chemisorption on the substrate surface. Among these clusters some will reach a critical size such that their Gibbs free energy will favour instead of loss of the other STO atoms. The contrary is true for the subcritical clusters.

Many simplifying assumptions are made to develop the mathematics of the model: i) the initial stage of chemisorption on the substrate N_0 sites is assumed to occur only for the first atom of the cluster; ii) the interaction of the cluster with the surface is assumed to be contained inside the surface energy and the misfit substrate-cluster strain energy contribution to the cluster formation Gibbs free energy; iii) the number of site N_0 and consequently the number of clusters is limited; iv) a certain time is considered to be necessary to grow a distribution of subcritical and critical clusters.

In line with the extensive work done on this subject, and in particular by Kaschiev [7], an evolution equation for the formation rate of clusters, composed of n atoms ($1 < n < \infty$) on the substrate surface, can be defined and solved. The rate of formation of the n-sized clusters with dimensions corresponding to the critical clusters provides, by definition, the rate nucleation. After several mathematical development and suitable approximations reported elsewhere [7], we get the main result of this work for the nucleation rate:

$$dN/dt = \beta N_0\exp(-\tau/t_b)\exp(-\beta t_b)$$
(13)

This is an expression similar to Eq. (10) but with an extra term representing the exponential time dependence, varying very rapidly for short times, leading to a zero rate of nucleation, at $t = 0$, explaining the time behaviour of the experimentally observed nucleation rates. The extra term accounts for an incubation time (τ) for the nucleation rate, which is associated with the formation time of a critical nucleus. It can be shown that this time is given by:

$$\tau = \tau_0\exp(E_a/kT)$$
(14)

where E_a is the activation energy of the strontium titanate atoms in passing from the gaseous to the solid phase; τ_0 is a slow temperature-dependent time period, which is directly proportional to the temperature and the cluster sur-

face energy, while it is inversely proportional to the square of the condensation Gibbs free energy and to the interface misfit strain energy. The experimental findings show that τ is well-represented by Eq. (14), with value of $E_a = 0.7$ eV and $\tau_0 = 567$ s. From the previous discussion, it appears that the incubation time is largely dependent on the substrate properties.

4. Conclusions

Atomic force microscopy is an emerging and powerful technique for surface morphological observations and it has been employed to study the nanoscale microstructure and surface features of $SrTiO_3$ thin films grown by pulsed laser ablation deposition. The nucleation rate has been derived from the strontium titanate particle size distribution, observed by atomic force microscopy. The derived nucleation rate shows a maximum after a certain growth time: it is negligible at the start and decays at longer times. A kinetic model has been derived to explain the time behaviour for the nucleation rate which includes the following main features: i) nucleation occurs on sites present and/or induced by pre-treatment on the substrate surface; ii) the nucleation process needs a temperature dependent incubation time to grow critically sized $SrTiO_3$ clusters on the Si surface.

The temperature dependence of the nucleation rate seems to agree with that is expected. The incubation time is largely temperature-dependent and decreases rapidly at high temperature. Possibly, it is a function of the misfit

strain energy between the Si substrate surface and the $SrTiO_3$ nuclei. However, more experimental and theoretical work are needed to confirm this model and to check the nucleation trends on different substrates.

Acknowledgements

References

[1] X.D. Wu, D. Dijkamp, S.B. Ogale, A. Inam, E.W. Chase, P.F. Miceli, C.C. Chang, J.M. Tarascon, T. Venkatesan, Appl. Phys. Lett. 51 (1987) 861.
[2] T. Sakuma, S. Yamamichi, S. Matsubara, H. Yamaguchi, Y. Miyasaka, Appl. Phys. Lett. 57 (1990) 2431.
[3] J. Gerblinger, H. Meixner, J. Appl. Phys. 67 (1990) 7453.
[4] E. Wiener-Avner, G.L. Kerber, J.E. McFall, J.W. Spargo, A.G. Toth, Appl. Phys. Lett. 56 (1990) 1802.
[5] F. Sánchez, M. Varela, X. Queralt, R. Aguilar, J.L. Morenza, Appl. Phys. Lett. 61 (1992) 2228.
[6] G. Yu, S.T. Lee, J.K.L. Lai, L. Ngai, J. Appl. Phys. 81 (1997) 89.
[7] D. Kaschiev, Surf. Sci. 14 (1969) 209.