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TIME RESOLVED REFLECTIVITY MEASUREMENTS IN Pb-IMPLANTED $SrTiO_3$

J. C. McCallum, J. Rankin, C. W. White, and L. A. Boatner

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TIME RESOLVED REFLECTIVITY MEASUREMENTS IN Pb-IMPLANTED $SrTiO_3$*

J. C. McCallum, J. Rankin, C. W. White, and L. A. Boatner
Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

Abstract

Time resolved optical reflectivity (TRR) is a simple and elegant technique for dynamically monitoring the interface motion that occurs during crystallisation of thin films and amorphous layers on crystalline substrates. This in situ technique has enabled measurements of the solid-phase epitaxial regrowth rate of amorphous silicon layers produced by ion implantation to be extended by over five orders of magnitude to rates in excess of 10^6 Å/s.[1] TRR is also well suited to measurements of crystallisation kinetics in ion-implanted ceramic oxides. In the present work, the technique is used to directly monitor the regrowth during thermal annealing of amorphous layers produced by ion implantation in the crystalline ceramic oxide $SrTiO_3$. In particular, the effect of ambient water vapour on the epitaxial regrowth rate of amorphous layers in these materials has been examined. This study provides new insight into the role of water in regrowth of materials of this nature and clearly illustrates the utility of TRR in measurements of crystallisation rates in ceramic oxides.

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INTRODUCTION

The development of the technique of time resolved reflectivity (TRR) allowed significant progress to be made in the study of solid-phase epitaxial crystallisation (SPE) of ion-implanted silicon and deposited amorphous silicon films [1–4]. This in situ technique utilises the optical interference which occurs between light reflected from the sample surface and from the underlying growth interface to provide a continuous record of the interface position as a function of time during recrystallisation. Not only has TRR allowed measurements of the SPE rate of amorphous layers produced in Si by ion implantation to be extended over a broad range of temperatures and growth velocities, it has also allowed the effects of implanted impurities on the epitaxial growth rate and the competition between random crystallisation and SPE to be examined in detail [1].

Time resolved reflectivity can also be profitably applied to studies of crystalline ceramics. In recent years, there has been increasing interest in ion implantation and thermal annealing processes in ceramic materials [5]. Ion implantation has been investigated as a means to produce favourable changes in the mechanical or optical properties of several different ceramic oxides [5–7]. In a number of these materials, it has been demonstrated that the amorphous layer produced by ion implantation can be regrown by solid-phase epitaxy [5]. It has also been noted that for materials such as $LiNbO_3$ [7], $SrTiO_3$, $CaTiO_3$ [8], and fused quartz [9,10], the presence of water vapour in the annealing environment tends to enhance the growth rate associated with the amorphous-crystalline phase change. Time resolved reflectivity offers a convenient means of characterising these growth processes in ceramic oxides. In this paper, the concept of TRR as applied to measurements in ceramic oxides is introduced and data are presented that illustrate the utility of TRR in investigating the effect of water vapour on the SPE rate of $SrTiO_3$.

EXPERIMENTAL

Single crystals of (100) $SrTiO_3$ (a cubic perovskite) were implanted with either 540 keV or 2.0 MeV Pb ions to a dose of $1 \times 10^{15}/cm^2$ at liquid nitrogen temperature. Cross-section transmission electron microscopy and Rutherford backscattering spectrometry (RBS)/ion channeling measurements showed that these implantation conditions were sufficient to fully amorphise the surface region of the $SrTiO_3$ crystals. In the case of the 540 keV Pb implant, the amorphous layer thickness was found to be $\sim$ 1800 Å and for 2.0 MeV Pb an amorphous layer $\sim$ 5900 Å was produced. Previous investigations of amorphous layers produced in $SrTiO_3$ by Pb implantation have shown that the layers regrow by solid-phase epitaxy at temperatures in the range of 250°C and that the Pb is located substitutionally on lattice sites in the recrystallised material [5].

For the TRR measurements, the implanted crystals were thermally annealed on a resistively heated stage which was enclosed in a stainless steel chamber to provide a controlled annealing environment. The chamber was fitted with a quartz window so that the He-Ne probe laser which provides the reflectivity signal could be reflected off the sample. The samples were introduced into the chamber via an interlock system so that the annealing environment could be maintained over a series of anneals. The data presented in this paper compares the epitaxial growth behaviour of two different annealing environments: (a) dry N_2 gas and (b) $N_2 + 2.7\%$ H_2O.

RESULTS AND DISCUSSION

The configuration used for the time resolved reflectivity measurements is represented schematically in Fig. 1. A He-Ne probe laser beam reflects off the sample into a photodiode. At the sample, optical reflections arise at both the air/amorphous interface and the crystal/amorphous interface if the refractive index is discontinuous at these boundaries. For a plane wave incident at angle θ_1 to the surface normal in this three-layer system the reflectivity, R, as a function of amorphous layer thickness, z, is given by [1,11]:

$$R = \left| \frac{r_{12} + r_{23} e^{-\alpha z cos\theta_1} e^{-2ikz cos\theta_1}}{1 + r_{12} r_{23} e^{-\alpha z cos\theta_1} e^{-2ikz cos\theta_1}} \right|^2$$

where $\alpha = (4\pi/\lambda)\mathrm{Im}(n_2)$ is the absorption coefficient and $k = (2\pi/\lambda)\mathrm{Re}(n_2)$ is the wave number in the amorphous layer. For a He-Ne laser, $\lambda = 6328$ Å. The reflection coefficients r_{12} and r_{23} at the air/amorphous and the amorphous/crystalline interface are given by:

$$r_{ij} = \frac{n_i cos\theta_i - n_j cos\theta_j}{n_i cos\theta_i + n_j cos\theta_j}$$

where n_i, n_j are the complex refractive indices and θ_i, θ_j are the beam angles to the surface normal in layers i and j. As the amorphous/crystalline growth interface proceeds towards the surface the intensity of the reflected signal varies, as indicated in Fig. 1. The wave number, k, in the amorphous layer is responsible for the periodicity of the oscillations and the absorption coefficient, α, causes damping of the signal amplitude with increasing amorphous layer thickness.

Fig. 2 shows the measured reflectivity trace for an anneal at 445°C in dry N_2 of a $SrTiO_3$ sample implanted with Pb(2.0 MeV, $1 \times 10^{15}/cm^2$). The signal variation in the trace corresponds to complete epitaxial recrystallisation of the amorphous layer (originally $\sim$ 5900Å thick) in a time period of $\sim$ 10 minutes. The average interface velocity during the anneal was $\sim$ 11Å/s. The oscillatory behaviour of the reflectivity signal is clearly evident, however, the amplitude of the signal does not damp monotonically with increasing amorphous layer thickness (decreasing time) as would be expected from the discussion above. Instead, the signal amplitude is at first damped and then it increases again. This behaviour suggests that the sample is not well described by the simple three-layer model presented above. Ellipsometry techniques were used to attempt to measure a complex refractive index for the implanted layer and the conclusion was drawn that the refractive index may not be constant throughout the amorphous layer but instead may vary with depth (presumably as a function of the Pb concentration profile). Without knowing the dependence of the refractive index on depth we cannot fully deconvolute the reflectivity trace to produce a depth versus time profile. However, the general form of the reflectivity trace is observed to be the same from sample to sample and we have used RBS to calibrate the signal at a number of depths. The depths corresponding to various stages in the regrowth are plotted above the trace in Fig. 2. These values can be used to arrive at the average interface velocity over each depth interval.

The reflectivity trace in Fig. 3 is for an anneal at 365°C in dry N_2 of a $SrTiO_3$ sample implanted with Pb(540 keV, $1 \times 10^{15}/cm^2$). The as-implanted amorphous layer thickness is $\sim$ 1800 Å. By using RBS to provide a depth calibration for the trace, the three average velocities, v_1 for 1800–1300 Å, v_2 for 1300–600 Å, and v_3 for 600–0 Å, can be measured. The data presented in Figs. 4 and 5 were obtained in this manner.

The reflectivity traces presented in Fig. 4 graphically illustrate the effect of water vapour on the epitaxial growth velocity in $SrTiO_3$. Both traces are for Pb(540.0 MeV, $1 \times 10^{15}/cm^2$) implanted $SrTiO_3$ samples annealed at 328°C. The solid curve is for a sample annealed in dry N_2 and the dashed curve is for a sample annealed in N_2 + 2.8% H_2O. At this annealing temperature, the growth velocity in the presence of 2.8% water vapour is approximately 15 times greater than that observed in dry N_2. A similar growth rate enhancement in the presence of water vapour has been observed during crystallisation of fused silica into quartz [9,10]. In those measurements, the dependence of the regrowth rate on hydroxyl or water vapour concentration could be described by a linear term in the pre-exponential factor of the growth velocity equation. The water was thought to act as a catalyst through involvement of hydroxyl groups in the configurational rearrangements responsible for crystallisation at the growth interface.

Time resolved reflectivity has been used to investigate the temperature dependence of the epitaxial growth rate in Pb implanted $SrTiO_3$ for anneals in dry N_2 and in N_2 + 2.7% H_2O. In Fig. 5, the growth velocities obtained from these measurements are plotted as a function of 1/kT. In the case of the dry N_2 anneals (squares), the growth velocity was found to be essentially constant throughout the anneal, i.e., the three growth velocities (Fig. 3) obtained from the TRR trace were approximately equal, $v_1 = v_2 = v_3$, in each case. The growth velocities plotted in Fig. 5 for dry N_2 are the average velocities and the error bars reflect the spread in the measured velocities. In most cases, the error bars are smaller than the symbols used to represent the data. Assuming an Arrhenius-type dependence of the growth velocity, the equation for the growth velocity can be written as $v = v_0\exp(-E_a/kT)$. Applying this equation to the dry N_2 data and using least-squares fitting techniques yields values of $v_0 = 3.0 \times 10^9$ Å/s, $E_a = 1.21$ eV. The fit to the data is shown by the solid line.

For the anneals in N_2 + 2.7% H_2O, the growth velocity was not constant but instead it tended to increase as the growth interface proceeded towards the surface. In general, the growth velocity, v_1, over the depth range 1800–1300 Å was found to be considerably lower than the growth velocities, v_2 and v_3, nearer to the surface. In general, the velocities

v_2 and v_3 were found to be approximately equal. This growth behaviour is similar to that reported for regrowth of Pb implanted $SrTiO_3$ samples when anneals were performed in air [5]. In those measurements, two stages were observed in the regrowth of the amorphous layers. There was an initial stage, or induction period, of slow regrowth which was then followed by a fast stage where a higher growth velocity was observed. In Fig. 5, two sets of growth velocities have been plotted for the TRR measurements of $SrTiO_3$ samples annealed in N_2 + 2.7% H_2O: the slow growth velocity v_1 (circles) over the depth range of 1800–1300 Å, and the average growth velocity v_{23} (triangles) for depths in the range 1300–0 Å. Again, the error bars represent the spread in the measured velocities and are generally smaller than the symbol size. A least-squares fit to the data for the slow growth velocity, v_1, produces values of $v_0 = 2.1 \times 10^{10}$ Å/s and $E_a = 1.21$ eV, i.e., the activation energy E_a is the same as that obtained for the dry N_2 anneals but the pre-exponential term is different. This behaviour is similar to that observed in the studies of crystallisation of fused silica into quartz, as discussed above. The data for the fast velocity, v_{23}, have been fitted with the same activation energy, $E_a = 1.21$ eV, and the pre-exponential becomes $v_0 = 5.1 \times 10^{10}$ Å/s. The fit is not as good as that obtained in the other two cases but there is also a greater scatter in the data. At this stage, the exact nature of the species which diffuses through the amorphous layer to the growth interface and is responsible for the enhancement of the regrowth rate in $SrTiO_3$ when water is present in the annealing environment is not known (presumably it is OH^- or H^+). The variation in the growth velocity for anneals in the presence of water vapour is most likely associated with the time required for the diffusing species to reach the growth interface. This is being investigated further.

The data presented in this paper clearly illustrates the manner in which time resolved reflectivity can be profitably applied to measurements of crystallisation behaviour in ceramic materials. A full discussion of the implications of the annealing results presented here is beyond the scope of this paper and will appear in a subsequent publication.

CONCLUSIONS

Time resolved reflectivity can be used to obtain valuable information about recrystallisation processes in ceramic oxides. In the case of $SrTiO_3$, TRR has allowed the effect of water vapour on the regrowth velocity to be studied in some detail. At present, the functional form of the refractive index in amorphous $SrTiO_3$ implanted with Pb is not known, however, the reflectivity signal is well-behaved from sample to sample and RBS can be used to calibrate the reflectivity trace. The functional form of the refractive index is currently being investigated.

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FIGURE CAPTIONS

Fig. 1. A schematic representation of the configuration used in time resolved reflectivity measurements. A He-Ne probe laser beam reflects off the sample into a detector. Interference between the signals reflected at the air/amorphous interface and at the underlying amorphous/crystal interface gives rise to oscillations in the detected signal as the growth interface advances towards the sample surface.

Fig. 2. The reflectivity trace for an anneal at 445°C in dry N_2 of a $SrTiO_3$ sample implanted with Pb(2.0 MeV, $1 \times 10^{15}/cm^2$). The signal variation in the trace corresponds to complete epitaxial recrystallisation of the amorphous layer (originally $\sim$ 5900 Å thick) in a time period of $\sim$ 10 minutes. RBS was used to measure the amorphous layer thicknesses corresponding to the positions indicated on the trace.

Fig. 3. The reflectivity trace for an anneal at 365°C in dry N_2 of a $SrTiO_3$ sample implanted with Pb(540 keV, $1 \times 10^{15}/cm^2$). The as-implanted amorphous layer thickness is $\sim$ 1800 Å. By using RBS to provide a depth calibration for the trace, the three average velocities, v_1 for 1800—1300 Å, v_2 for 1300—600 Å, and v_3 for 600—0 Å, can be measured.

Fig. 4. The reflectivity traces obtained for annealing at 328°C of two $SrTiO_3$ samples implanted with Pb(2.0 MeV, $1 \times 10^{15}/cm^2$). The solid curve is for the sample annealed in dry N_2 and the dashed curve is for the sample annealed in $N_2 + 2.8\%$ H_2O. The presence of water vapour in the annealing environment enhances the recrystallisation rate by a factor of $\sim$ 15.

Fig. 5. The growth velocity plotted as a function of 1/kT for TRR measurements on Pb implanted $SrTiO_3$ samples annealed at various temperatures in dry N_2 (squares) or in N_2 + 2.7% H_2O (circles and triangles). At a given temperature, the growth velocity was found to be essentially constant for samples annealed in dry N_2. In N_2 + 2.7% H_2O the growth velocity was found to increase as the growth interface proceeded towards the surface. The growth velocity v_1 is the average interface velocity over the depth range of 1800—1300 Å, and v_{23} corresponds to the depth range of 1300—0 Å.

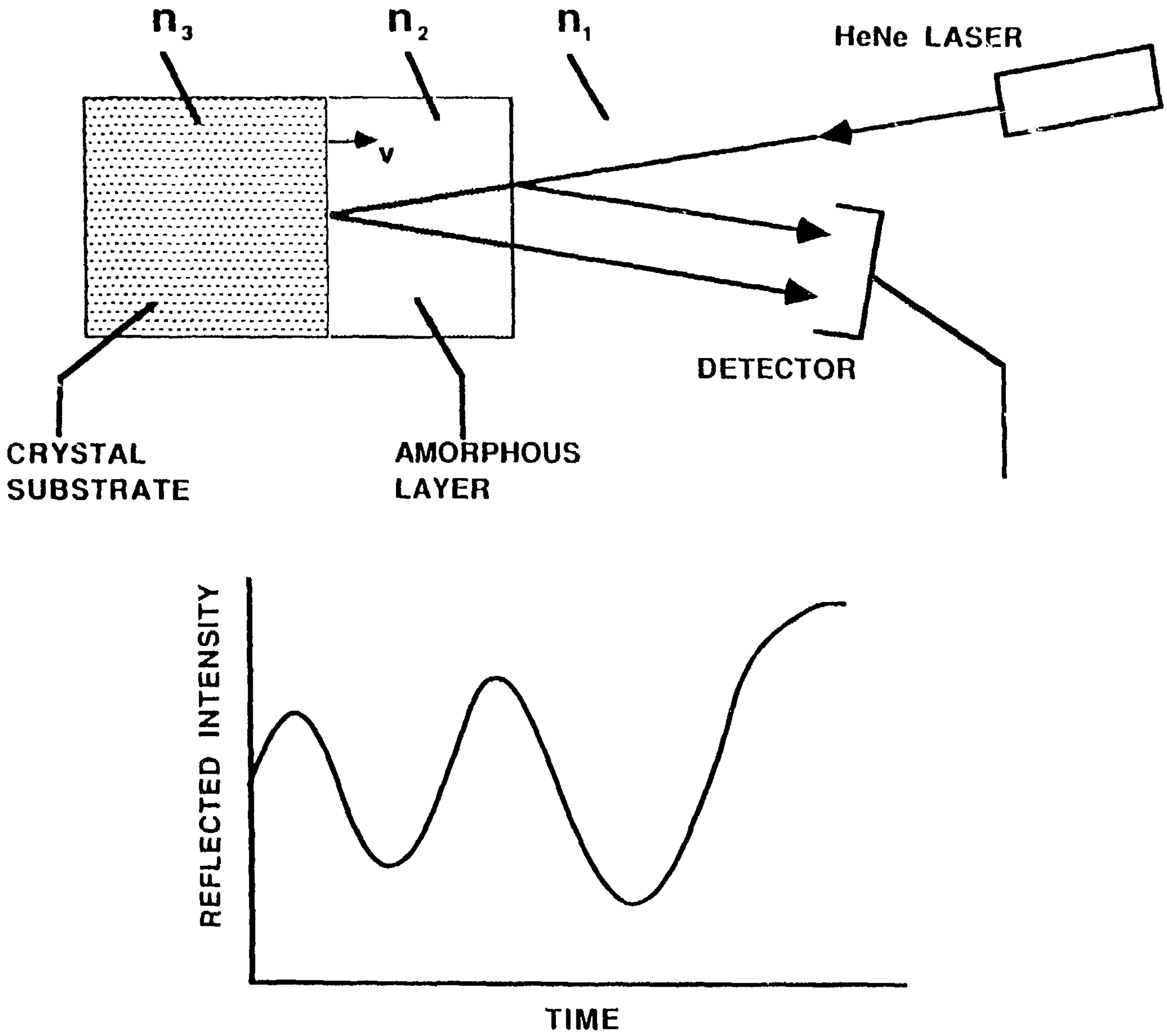
n_3
n_2
n_1
HeNe LASER
v
DETECTOR
CRYSTAL SUBSTRATE
AMORPHOUS LAYER
REFLECTED INTENSITY
TIME

FIG 1

ORNL-DWG 89-12490

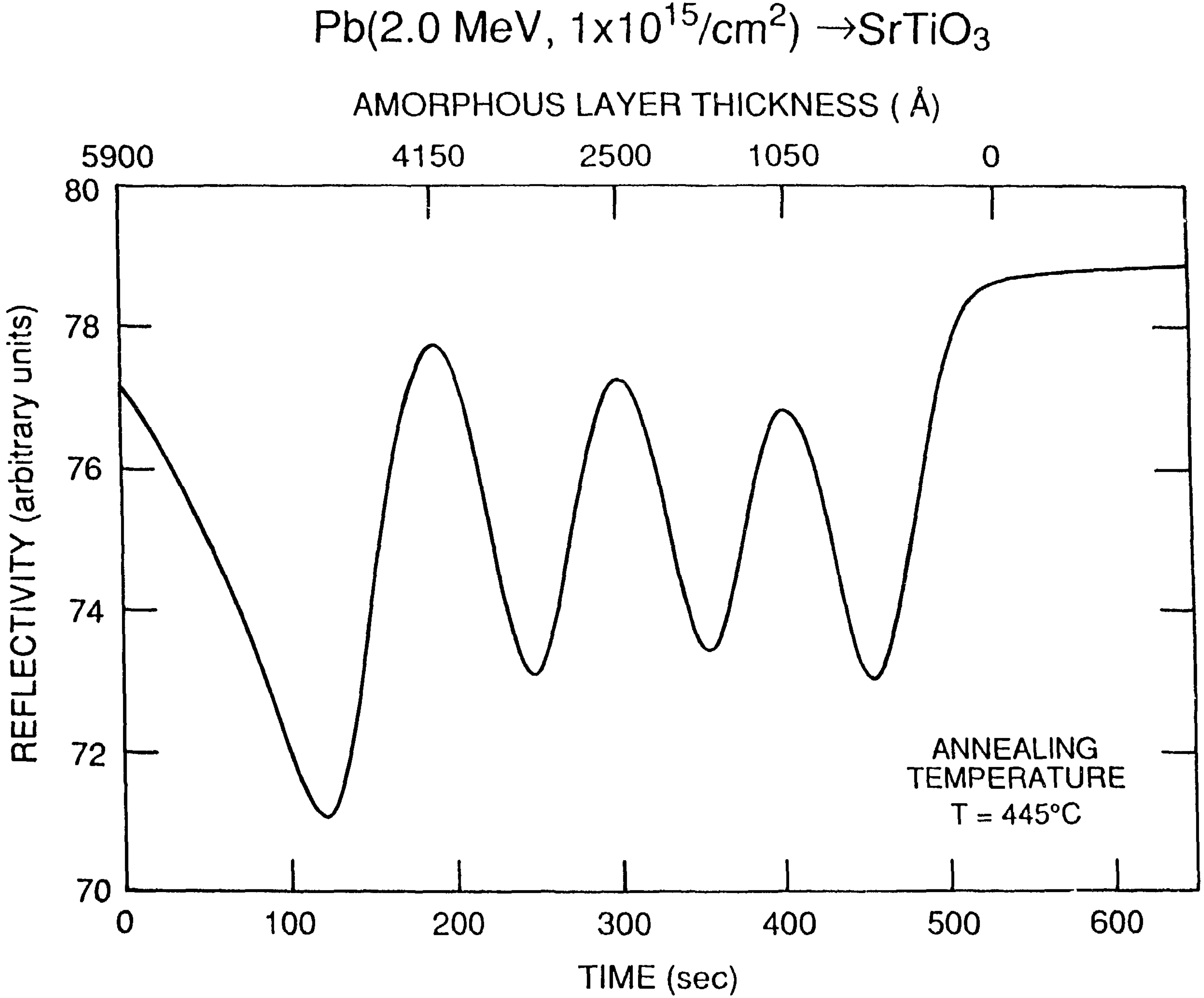

FIG 2

ORNL-DWG 89-12491

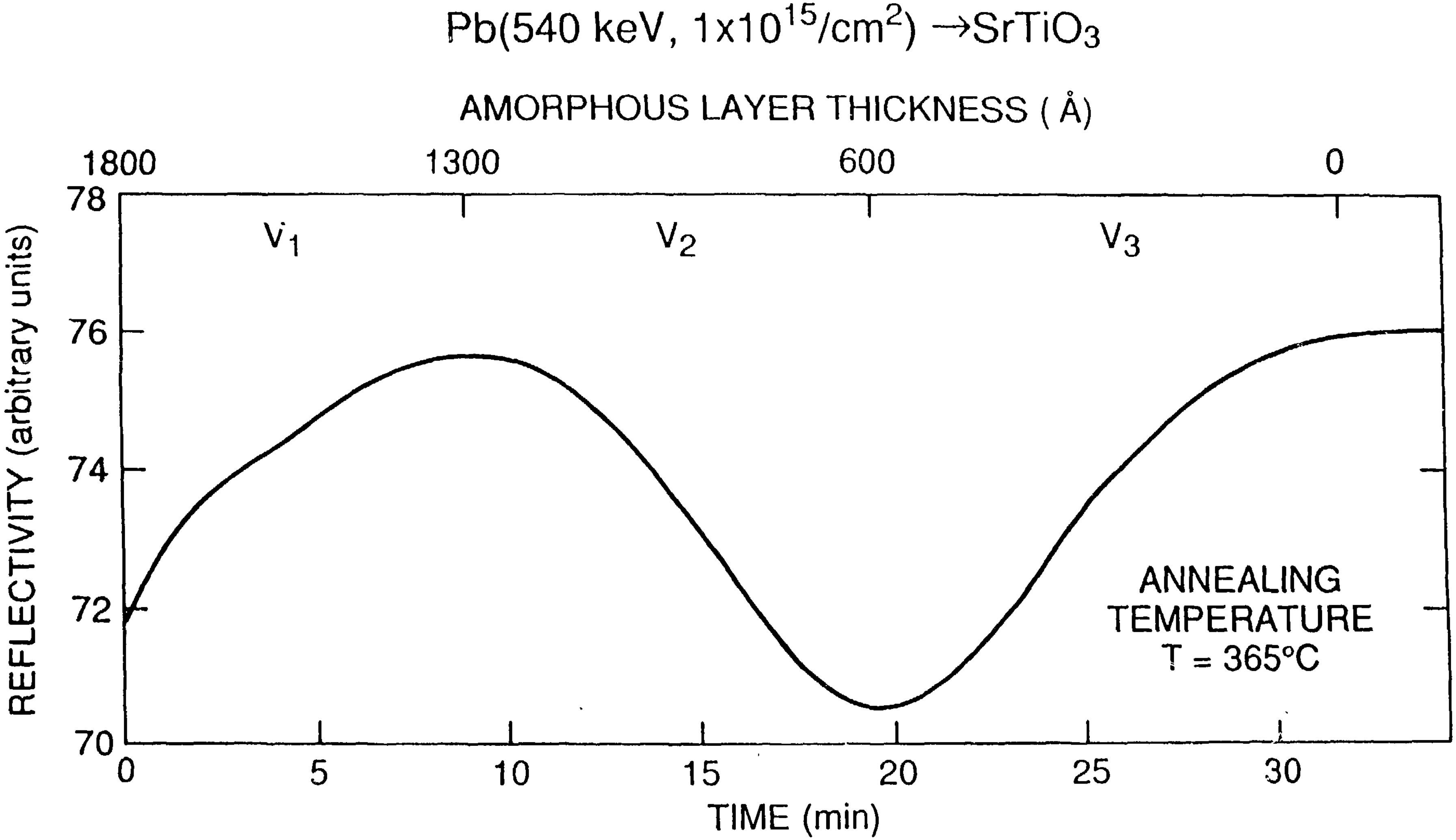

FIG 3

ORNL-DWG 89M-9252

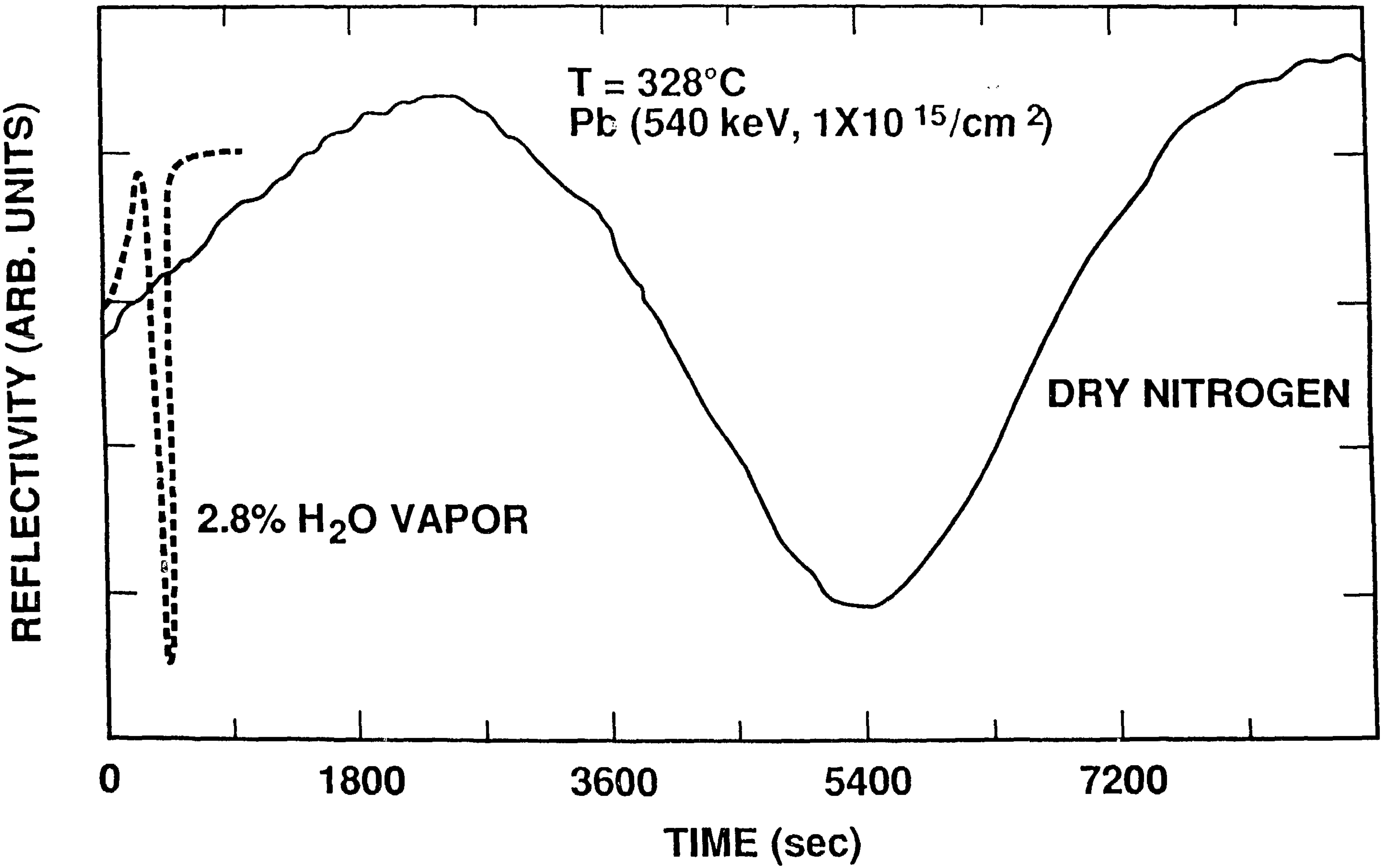

FIG. 4

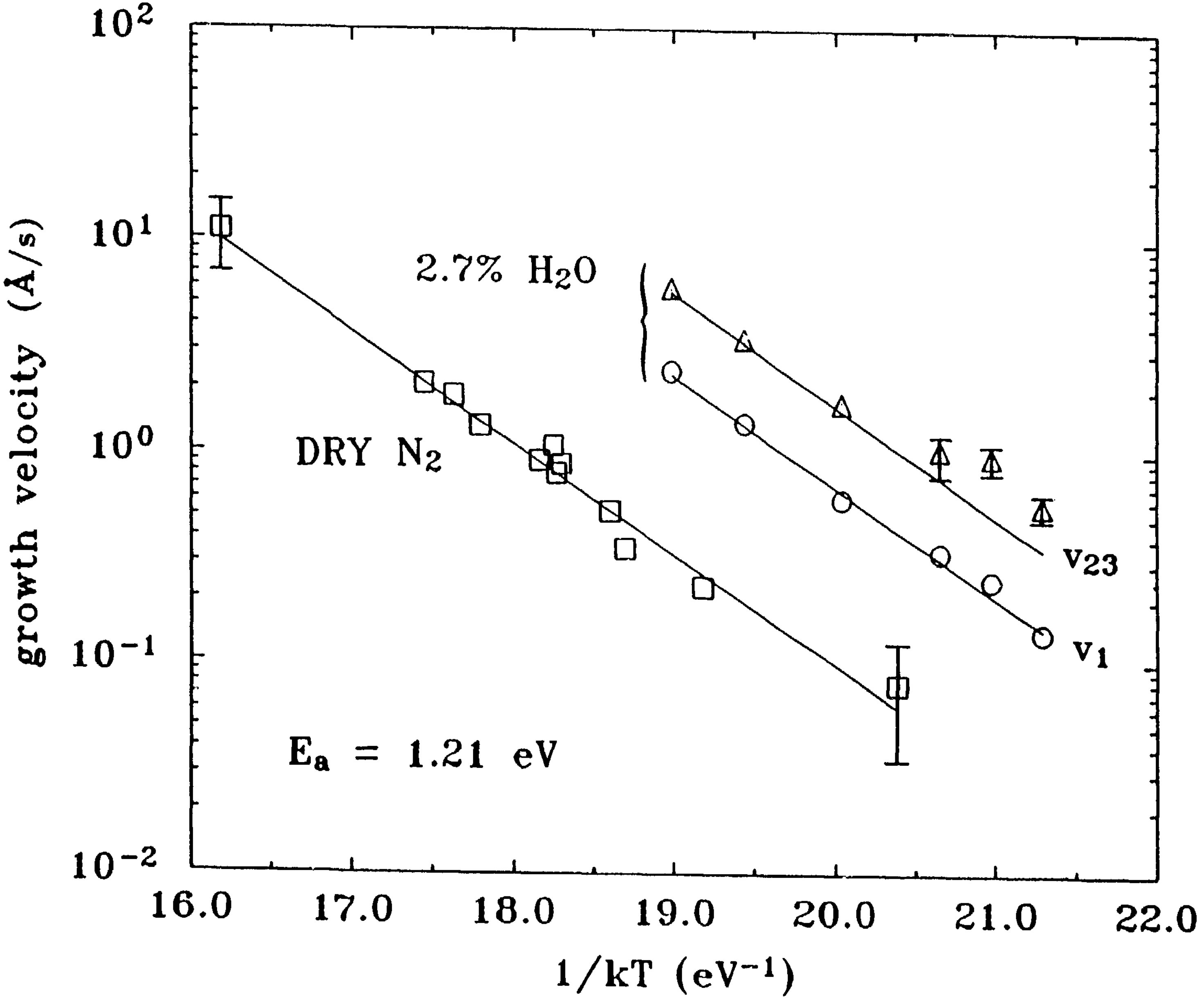
10^2
10^1
10^0
10^-1
10^-2
growth velocity (Å/s)
16.0
17.0
18.0
19.0
20.0
21.0
22.0
1/kT (eV^-1)
2.7% H2O
DRY N2
Ea = 1.21 eV
v23
v1

FIG. 5