Is the nucleation and coalescence behavior in the growth of a-Si:H films prepared by the CAT-CVD different?

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Abstract

This paper reports the results of detailed experiments carried out to understand the growth of a-Si:H films deposited by thermocatalytic chemical vapor deposition (TCCVD) at different substrate temperatures \( T_s \). Kinetic ellipsometry data reveal that the growth kinetics drastically changes as \( T_s \) is increased from 110 to 450°C. Although nucleation occurs at all \( T_s \), a major difference is observed in the coalescence behavior. At the lowest \( T_s \), no trace of coalescence is reflected in the data. In the intermediate \( T_s \) region, incomplete or partial coalescence introduces the lobe/cusp pattern in the \( (\langle e_1 \rangle, \langle e_2 \rangle) \) curve, while above 350°C, complete coalescence leads to the presence of a loop in the \( (\langle e_1 \rangle, \langle e_2 \rangle) \) data. We attribute this change in the \( (\langle e_1 \rangle, \langle e_2 \rangle) \) trajectory to a systematic variation in the surface reactivity and hydrogen coverage with increasing \( T_s \).

Keywords: Amorphous materials; Chemical vapor deposition (CVD); Deposition process

1. Introduction

The dependence of the physical and opto-electronic properties of hydrogenated amorphous silicon (a-Si:H) films deposited by either glow discharge (g.d.), reactive sputtering, or more recently, the thermo catalytic chemical vapor deposition (TCCVD), also called hot-wire (HW) deposition techniques on the substrate temperature \( T_s \) has been extensively studied [1–4]. It is now well accepted that for the g.d. method at low \( T_s \) (<150°C), columnar growth occurs and the film contains significant hydrogen in the SiH\(_2\) mode and shows poor electronic properties. On the other hand, at high \( T_s \), the hydrogen content is insufficient to achieve complete defect passivation and relieve the strain in the network, and so again the films are not of device quality. Thus, device-quality films can be grown over a limited temperature range. However, the TCCVD technique has yielded device-quality films with very low hydrogen content deposited at quite high \( T_s \) (400°C) [5,6].

Apart from the hydrogen distribution, it has been proposed that the growth kinetics during the crucial initial stages of film deposition affects the quality of films with respect to its microstructure and defect density. This proposition comes from the results of the kinetic ellipsometry (KE) studies of Collins and co-workers performed during the growth of g.d. a-Si:H under different deposition conditions [7–10]. These studies reveal that the convergence of initial nucleation clusters, which occurs above a certain \( T_s \) \((T_s=225°C)\), could be responsible for the growth of a film with uniform microstructure and good electronic properties. This phenomenon is reflected as a lobe/cusp feature in the \( (\langle e_1 \rangle, \langle e_2 \rangle) \) curve of in situ KE, and is present only for depositions above \( T_s=225°C \) and absent at lower \( T_s \) values. In light of these observations, it was pertinent to carry out in situ KE studies of TCCVD a-Si:H films deposited at different \( T_s \) values. Moreover, scant knowledge about the growth process of the TCCVD a-Si:H films exists at present, and it seems quite likely that since the TCCVD technique involves a different dissociation mechanism with minimal ion densities, the
growth kinetics are different compared to the g.d.
method.
In this paper we report in the effect of variation of
$T_s$ on the growth kinetics of TCCVD a-Si:H films
deposited on crystalline silicon (c-Si) substrates. It is
observed that the initial growth at different $T_s$ shows a
significant variation in the nucleation and coalescence
of the nucleation clusters before homogeneous growth
takes over. As a result, the microstructure of the films
in terms of density and surface roughness is affected, as
is evident in the spectroscopic data.

2. Experimental

The a-Si:H $i$-layers were deposited on c-Si with its
native oxide in a UHV reactor using a 0.5-mm-diameter
tantalum filament. The substrates were mounted on a
vertical substrate holder and an ‘M’-shaped filament
was mounted parallel to this at a distance of 5 cm. In
situ kinetic ellipsometric (KE) measurements, where the
complex dielectric function $\langle \epsilon \rangle = \langle \epsilon_i \rangle + i\langle \epsilon_s \rangle$ is measured
in terms of the change of the polarization of light
reflected at the sample surface, was performed as
described in [11]. The KE measurements were carried
using 3.4-eV incident photon-beam energy. The spec-
trum of a deposited sample was measured with the
filament off and the result obtained was cross-checked
against a measurement with a heated virgin filament,
with no difference found between the two. The process
parameters, such as filament temperature $T_{Fi}=1500^\circ$C,
gas pressure $p=20$ mtorr, undiluted silane flow $F=15$
sccm and filament-to-substrate distance $=5$ cm, were
held constant, and only the substrate temperature $T_s$
was varied from 110 to 450$^\circ$C. The $T_{Fi}$ was measured with
the help of an optical pyrometer (IRCON).

3. Results and discussion

One simple and effective way to understand the
kinetic ellipsometry data is to plot the imaginary part
$\langle \epsilon_s \rangle$ of the measured dielectric constant $\epsilon$
as a function of the real part $\langle \epsilon_i \rangle$, with time as the implicit parameter. This representation enables a quick idea to be obtained
about the important material properties, such as the
Si–Si bond density and the surface roughness of the
converging film. In order to achieve interface sensitivity,
the measurements are carried using 3.4-eV incident
photon-beam energy. At this energy, the ellipsometric
trajectories provide information about nucleation and
coalescence occurring at the substrate film interface
during the initial phase of film deposition. In order to
determine the bulk $i$-layer properties in terms of the
Si–Si bond density and surface layer roughness, spec-
 troscopic ellipsometry is performed at room temperature
on 1-$\mu$m-thick films after deposition over the energy
range 2.5–5 eV. The maximum value and the peak
position of $\langle \epsilon_s \rangle$ in the spectroscopic data are related to
the Si–Si bond density and the surface roughness,
respectively. In general, a higher $\langle \epsilon_s \rangle$ value reflects a
denser film, while deviation of the peak position from
3.6 eV to lower values is a measure of the surface
roughness. Fig. 1 shows the KE $\langle \epsilon_i,\epsilon_s \rangle$ trajectory
for the film deposited at the highest $T_s$ of 450$^\circ$C, which
indicates the presence of a distinct loop before the
convergence. Drevillon [12] obtained a similar curve for
g.d. a-Si:H samples grown at 300$^\circ$C, and the data could
be fitted with growth involving nucleation (A–B), coa-
lescence at a certain rate (B–C) and further homogeneous
growth with surface roughness (C–D). Thus, it seems
that the nature of the initial growth in TCCVD a-Si:H
films ($T_s=450^\circ$C) is quite similar to the g.d. films
($T_s=300^\circ$C), however, with a different rate of nuclea-
tion and coalescence. The spectroscopic data (Fig. 2,
$T_s=450^\circ$C) reveal that a very high-density film, with
very low surface roughness is formed at this $T_s$. In Fig.
3, we show the trajectory for the film deposited at
375$^\circ$C, which again reflects the loop pattern before
convergence, indicating complete coalescence of the
nuclei. However, the radius of the loop is much smaller
in this case, and could be fitted with a lower coalescence
rate after the initial nucleation. This is logical, as the
lower $T_s$ would certainly reduce the surface mobility of
the ad-atoms, and hence result in a low rate of coales-
cence. As a result, the final film shows a slightly lower
density (Fig. 2, $T_s=375^\circ$C).

Various attempts to model the initial growth of a-Si:H
films deposited by the RF glow discharge technique
have been made [12,13]. These models consider differ-
ent possibilities of nucleation occurring through the

![Fig. 1. Kinetic ellipsometry trajectory for TCCD a-Si:H film deposited on c-Si substrate. The upper right end of the curve marks the start of the data and corresponds to the dielectric values of the substrate at the deposition temperature $T_c$.](image)
formation of nuclei with different shapes, such as hemispherical, disc-like, or cylindrical. These nuclei are initially spaced apart and the space between them gets filled up either by coalescence or by further adsorption, with further growth of the film. Which of these predominate will depend on the substrate temperature. In addition, different amounts of fixed surface roughness in the initial growth, which increase linearly with thickness, have been considered. Thirdly, the possibility of void formation and trapping was also included in the model calculations, which are based on the Bruggeman effective medium approximation (EMA). Thus, a model calculation which considers formation of disc-like nuclei, spaced apart in the initial stage with a fixed surface roughness, results in a lobe/cusp pattern as the space between the nuclei gets filled with further growth up to 50 Å. This filling process would depend on the mobility of the adsorbed atoms, and hence on the substrate temperature. A further decrease in $\langle \varepsilon_2 \rangle$ after the film has grown above 500 Å is due to the increased surface roughness, which increases linearly with thickness. In the discussion of the present results (for curves in Figs. 4–6), we have taken note of this model, since our data also reflect a lobe/cusp pattern in the KE trajectory curves.

Thus, the KE trajectory curve shown in Fig. 4 of the film deposited at 275°C is similar to that observed by Collins for g.d. films deposited at 250°C [13] and could be explained on the basis of the model discussed above. The final film shows a lower density and slightly higher surface roughness (Fig. 2, $T_s = 275°C$). In Fig. 5, we plot the KE trajectory for the film deposited at 200°C. It is evident that there is a very small but definite trace of a lobe in the trajectory. The final film shows a still
lower density and a higher surface roughness (Fig. 2, \( T_s = 200^\circ \text{C} \)). In Fig. 6, we plot the KE trajectory for \( T_s = 110^\circ \text{C} \), which indicates no trace of either the lobe or cusp. Two ways in which islands or clusters formed by the initial nucleation can grow are: (a) by direct addition from the vapor phase above the substrate (homogenous growth); and (b) migration across the substrate (coalescence). In the case of (a), the islands would grow more rapidly in height than in area, provided the deposition rate is high, the surface diffusion energy is large and \( T_s \) is low. Thus, the possibility of observing coalescence is minimal. Case (b) could occur only if the ad-atoms had a high surface mobility (say due to high \( T_s \)). Thus, for \( T_s = 110^\circ \text{C} \), homogenous growth of the film with no coalescence seems likely, ultimately yielding a film with very low density, as indicated by the extremely low value of \( \langle \varepsilon_2 \rangle \) in the spectroscopic data for this film (Fig. 2, \( T_s = 110^\circ \text{C} \)).

It should be noted that the appearance of the lobe in the intermediate \( T_s \) range, followed by its transformation to a loop pattern at higher \( T_s \), is a consequence of the increase in the coalescence rate at higher \( T_s \). The trends observed in the growth throughout the \( T_s \) range are completely justified on the basis of an increasing surface mobility of the ad-atoms with increasing \( T_s \). However, it is rather difficult to explain the exact way in which \( T_s \) and the hydrogen coverage of the surface affect the mobility of the initial nucleation clusters. These findings provide the exact situations for observation of both the loop and the lobe/cusp pattern in the growth trajectories of a-Si:H. Also, the results clearly elucidate how the initial layer, which grows up to the first 10s of Å, affects the microstructure of the final film.

4. Conclusion

A systematic study of the variation in the growth kinetics of TCCVD a-Si:H employing kinetic ellipsometry has been carried out. The results clearly show that the growth pattern changes from a lobe/cusp pattern, indicating nucleation and partial coalescence in the intermediate \( T_s \) region, to a loop for higher \( T_s \), indicating complete coalescence. None of these features are present at the lowest \( T_s \) value of \( 110^\circ \text{C} \), suggesting that these processes do not occur at such low \( T_s \). As a result, the films grown at low \( T_s \) have poor microstructure and electronic properties. The variation in the initial growth behavior at different \( T_s \) can be explained on the basis of an increase in the surface mobility with increasing \( T_s \), as well as a change in the hydrogen coverage of the surface.

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References