Solid state transitions during the growth of silicon by chemical vapour deposition

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SOLID STATE TRANSITIONS DURING THE GROWTH OF SILICON BY CHEMICAL VAPOUR DEPOSITION

A.M. BEERS, H.T.J.M. HINTZEN, J. BLOEM

RIM, Department of Solid State Chemistry, University of Nijmegen, Toernooiveld N3096, 6525 ED Nijmegen, The Netherlands

ABSTRACT

The crystalline-amorphous transition during chemical vapour deposition of silicon has been studied. Results are reported for growth from 2.3 vol% SiH4 in hydrogen at atmospheric pressure. From optical measurements two after-growth phenomena were discerned, viz. a change in emissivity below T = 678°C and a change in optical thickness below T = 772°C. Consistent with the mechanism of formation the observed optical phenomena are connected with differences in the structure of the deposited material and the related solid state transitions a-Si:H \(\rightarrow\) a-Si \(\rightarrow\) c-Si.

INTRODUCTION

The principle aim of this study is the investigation of the crystalline-amorphous transition of silicon during growth by Chemical Vapour Deposition (CVD) from silane SiH4. The temperatures reported1,2 for this transition are in the same range (600-700°C) as those for which appreciable crystallization of amorphous silicon upon annealing was reported3,4. Therefore, a simultaneous action of both the amorphous growth process and solid state crystallization might be conjectured in this temperature range.

In general, it should be acknowledged that although a material grows with a certain structure, after deposition the structure can be different because of after-growth solid-state anneal processes. In order to investigate the different processes which take place simultaneously the employment of optical techniques is inevitable as these can be applied in situ.

EXPERIMENTAL

Silicon films were deposited at surface temperatures between 560 and 800°C through pyrolytic decomposition of 2.3% SiH4 in hydrogen H2 at atmospheric pressure and an average linear gas velocity \(\sim\) 50 cm s\(^{-1}\). This CVD process was carried out in a horizontal watercooled reactor tube with the substrates placed on an rf heated graphite susceptor. Two independent optical techniques are applied.
continuously during growth:

(i) thermal radiation normally emitted by the specimen was received with a radiation pyrometer (bandwidth 1.9-2.6 μm); this measurement allows the determination of the surface temperature.

(ii) using an incident ray of monochromatic light (λ = 1.15 μm) the time-resolved optical reflectivity of the processed material was measured; this technique also allows the determination of the growth rate from the duration of the oscillations which occur as a result of optical interference between the rays reflected at the outer surface and at the interface with the substrate.

The emissivity measurements (i) started on polished monocrystalline silicon substrates and the rate of growth (method ii) was measured on a juxtaposed Si₃N₄ coated substrate; the (small) mutual temperature difference was corrected for. Growth rate R is directly proportional to the reciprocal of the oscillation period (τ⁻¹) with proportionality constant \(\lambda/2(n^2-n_0^2 \sin^2 \varphi_o)^{1/2} \approx 0.16 \ \mu m\), where for the relevant temperature range and wavelength the refractive index of the growing layer \(n \approx 3.7\); furthermore, \(n_0 \approx 1\) and the angle of incidence \(\varphi_o = 53^0\). The thickness of the deposited solid layers was approximately 1.6 μm corresponding to 10.2 ± 0.1 oscillations in the laser interference pattern.

EXPERIMENTAL RESULTS

The results of the measurements of growth rate R as a function of surface temperature T show that it varies continuously between 0.02 μm/min at 560°C and 2 μm/min at 800°C. In the thermal radiation measurements (i) as a function of surface temperature a change in the emissivity behaviour was found at \(T' = 678°C\). Below 678°C it was found that during growth the emissivity was higher than before growth. After the termination of growth, effected by discontinuing the flow of silane, a post-growth phenomenon was found in the gradual disappearance of the surplus emissivity if the specimen was kept at the same temperature in the same flow of hydrogen. The surplus emissivity as measured on a temperature scale amounted to 9°C at a growth temperature of about 570°C and was smaller the higher the growth temperature; above 678°C this emissivity phenomenon did not occur.

Also the laser interference technique (ii) offers evidence of after-growth processes. Well below \(T'\) at the lowest temperatures in the present experiments a very small effect was also noticeable in the laser interference pattern upon annealing directly after growth. It took the same length of time (a few minutes) for the laser interference signal to stabilize at a level corresponding to a smaller optical thickness of the layer as it took for the emissivity signal to regain its original level. This length of time was found to decrease and to approach zero for temperatures approaching \(T'\). However, around these temperatures
it took much longer to observe another and much larger effect: after the termina-

tion of growth the optical path length difference of the reflected rays was

found to decrease corresponding with up to about one oscillation in the laser

interference pattern before stabilization. For growth experiments at still

higher temperatures this amount, as well as the time involved to effect this

change, became progressively smaller until no such effect was apparent anymore

for growth temperatures above \( T^* = 772^\circ C \).

Measurement of the room temperature refractive indices \( n \) of the layers, which

were grown at temperatures above and below \( T^* \) and which were not intentionally

annealed, resulted in \( n = 3.45 \pm 0.10 \) (\( > T^* \)) and \( n = 3.51 \pm 0.20 \) (\( < T^* \)) using

the technique \(^6\) of interference of infrared light with wavelengths

\( 2.5 < \lambda < 5.0 \) \( \mu m \). In these measurements the thickness was determined by the

Tolansky technique.

DISCUSSION/CONCLUSIONS

In an analysis of the experimental results it should be recognized from the

outset that the observed "transition temperatures" refer to transitions during

growth. Therefore, the initial formation of solid material, unstable at the tem-

perature of growth, should be taken into account. The actual presence of such

transitions in these growth experiments is inferred from the optical phenomena

which were observed during and after growth: clearly the optical constants of

the material change through the action of solid state anneal processes. The

transitions related to the two transition temperatures reported are considered

to be different in kind because of the different effects reported for the emis-

sivity and laser interference measurements and the widely different transition

temperatures. Among the possible phase transformations recrystallization of the

thin solid layer can be excluded because this is known \(^7\) to occur at an appre-

ciable rate at much higher temperatures only. It is judged that the lower tem-

perature transition (\( \approx T' \)) is the decomposition of amorphous silicon hydride

and that the higher temperature transition (\( \approx T^* \)) is the crystallization of

amorphous silicon; these transitions (\( a-Si:H \rightarrow a-Si \), resp. \( a-Si \rightarrow c-Si \)) are

schematically represented in Fig. 1.

This interpretation is also compatible with recent views \(^8,9\) on the mechanism

of CVD of silicon from silane. At lower temperatures, hydrogen can be incorpor-

ated in the growing solid and hydrogenated amorphous silicon \( a-Si:H \) is formed.

However, if at higher temperatures hydrogen is not incorporated its concen-

tration on the solid surface during growth can still be high enough to prevent

crystalline deposition of silicon and amorphous silicon \( a-Si \) is formed.

The observed after-growth anneal phenomena can be interpreted accordingly.

The change in emissivity reported for the lower temperature range (\( < T' \))
Fig. 1. Schematic representation of the different forms of silicon that grow dependent on temperature in the present experiments. The arrows indicate solid state transitions that may occur during growth as well as upon prolonged annealing after the termination of growth.

correlates with a higher absorption coefficient of a-Si:H as compared to that of a-Si. After the termination of a-Si:H growth the disappearance of the surplus emissivity is now explained by the solid state decomposition reaction a-Si:H \( \rightarrow \) a-Si. In the laser interference signal the decrease of the optical path length difference of the reflected rays results from changes in layer thickness as well as refractive index: indeed, both thickness and refractive index decrease upon crystallization of amorphous silicon a-Si \( \rightarrow \) c-Si.

Work is in progress to quantify the present results and to establish experimentally the expected dependence of both transition temperatures on the rate of growth.

REFERENCES