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HYDROGEN INCORPORATION DURING DEPOSITION OF a-Si:H FROM AN INTENSE SOURCE OF SiH_3

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ABSTRACT

The incorporation of hydrogen during the fast deposition of a-Si:H from an expanding thermal arc is investigated by means of isotope labeling of the precursor gases silane and hydrogen. It is found that hydrogen in a-Si:H originates dominantly from the silyl radical. A small fraction of the hydrogen in a-Si:H is due to exchange reaction of atomic hydrogen in the plasma with hydrogen chemisorbed on the surface during growth.

INTRODUCTION

It is a well-known fact that the hydrogen content of a-Si:H is strongly related to its opto-electronic properties such as photorespons and defect density [1]. A better understanding of the hydrogen incorporation during deposition of a-Si:H is therefore important. Several authors have reported the dependence of the hydrogen content of a-Si:H on substrate temperature, growth rate, radical and ion composition of the plasma, etc. Despite this intensive research, a clear understanding of how hydrogen is incorporated is still lacking for the case where the silyl radical is considered to be the dominant radical leading to high quality film deposition (e.g. during RF PECVD). Matsuda et al. [2], e.g., have shown that for a-Si:H deposited from dominantly SiH_3, hydrogen incorporation only depends on the substrate temperature and is more or less independent of growth rate in the range from 0.01 to 1 nm/s. In contrast to this result, hydrogen dilution during the RF PECVD of a-Si:H leads to a lower hydrogen content at lower substrate temperature than without hydrogen dilution [3]. On other hand Street and others state that the hydrogen content depends on the hydrogen chemical potential which is determined partly by hydrogen in the plasma [4]. Moreover, Beyer et al. reported that the hydrogen content in a-Si:H could be varied over a wide range by plasma post-treatment in a hydrogen plasma [5]. This result shows that also other processes than processes during plasma deposition can influence the hydrogen content of a-Si:H.

In a previous paper we discussed the substrate temperature dependence of the hydrogen content, band gap, defect density and refractive index [6]. It was concluded that, apart from the plasma settings, the substrate temperature is a key parameter to obtain good quality a-Si:H at high deposition rates of 7-10 nm/s using the expanding thermal plasma set up. For example, it was reported that the hydrogen content and the defect density decrease with increasing temperature downto device quality values (7% and 5×10^{15} cm^{-3}, respectively). Since the silyl radical contains three hydrogen atoms and a-Si:H contains only about 10% hydrogen, it is interesting to investigate how hydrogen is incorporated. This becomes particularly interesting considering the fact that also atomic hydrogen is present in the plasma which can influence this incorporation.

In this paper we will present isotope labeling studies on the incorporation of hydrogen during the fast deposition of a-Si:H. Under conditions where the silyl radical is dominant, studies using H_2 and D_2 dilution of SiH_4 and SiD_4 plasma will be performed to determine the hydrogen and deuterium content as a function of the substrate temperature.

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DEPOSITION SETUP

The setup consists of a DC thermal arc plasma source and a low-pressure chamber (Fig. 1): plasma production and deposition are geometrically separated, and in that sense this method can be classified as Remote Plasma Deposition. The plasma is generated in a mixture of argon and hydrogen by a DC discharge (typically 50A, 100V) between three cathodes and an anode. As the

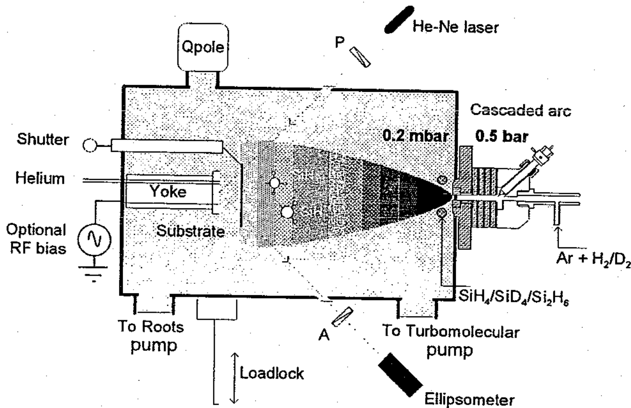

Fig. 1. The expanding thermal plasma set up.

arc is operated at a typical pressure of 0.5 bar, the plasma is close to local thermal equilibrium and characterized by a high electron density and low electron temperature ($n_e \approx 10^{22}$ m^{-3}, $T_e \approx 1$ eV). It flows into the deposition chamber through a parabolically shaped nozzle in the anode plate. In this case the flux of atomic hydrogen (deuterium) is several orders larger than the ion flux. The plasma expands supersonically into the deposition chamber (pressure typically 20 Pa), shocks and flows subsonically towards the substrate with a typical transport velocity of 10^3 m/s. At 32 cm downstream from the nozzle the substrate holder is positioned. In the argon/hydrogen plasma jet, typical downstream plasma parameters are an electron density of about 10^{17} m^{-3} and an electron temperature of about 0.2 eV. Pure silane is injected into the jet just behind the expansion nozzle through an injection ring. Due to the low electron temperature, the substrate self bias is less than 2 V: ion bombardment is negligible. It also rules out dissociation of silane by electron collisions; this is mainly attributed to hydrogen abstraction -primarily generating SiH_3- and to a sequence of dissociative charge exchange and consecutive dissociative recombination. In the experiments describe here the first process dominates.

Substrate temperature is controlled by means of resistive heaters inside the substrate holder and helium back flow between substrate and substrate holder. The temperature control is within 10 °C for temperatures in the range of 100 to 450 °C, as has been checked independently by infrared interferometry. A shutter can be positioned before the substrate during plasma start up and stabilization of the different gas flows.

The plasma condition used during the hydrogen incorporation study is given in Table 1. Under this condition hydrogen abstraction is considered to be dominant. a-Si:H was deposited on Corning glass 7059 and on crystalline silicon (<100>, resistivity 1-10 Ωcm). The hydrogen

content is determined using Elastic Recoil Detection Analysis (ERDA) with 4 MeV He^{++} particles generated

Table I. The plasma condition used during the experiments described

Argon flow	55 scc/s
Hydrogen flow	10 scc/s
Silane flow	10 scc/s
Chamber pressure	20 Pa
Arc current	55 A

with a cyclotron. More details on the ERDA can be found in Ref. [7]. Growth rates and refractive index are obtained using in situ HeNe ellipsometry at 632.8 nm.

RESULTS

Using the conditions as given in Table I a-Si:H is deposited with device quality properties as shown in Table II. Note that the values given apply to depositions made at 450 °C and a growth rate of about 11 nm/s. In Figs. 2 the total hydrogen content [H]+[D] as obtained using ERDA and the growth rate for three different flow compositions are given as a function of the substrate temperature. The three different flow compositions were: 1) settings as given in Table I, 2) settings as given in Table I except H_2 replaced by D_2 and 3) settings as given in Table I except SiH_4 is replaced SiD_4.

As can be concluded from Fig. 2a the total hydrogen content is more or less independent of the precursor gases used and depends strongly on the substrate temperature. However, the values obtained by the expanding thermal plasma are significantly higher than the values reported by Matsuda et al. [2] (growth rate independent up to 1 nm/s), suggesting a growth rate dependent hydrogen content when the growth rates exceeds a value of 1 nm/s. On the other hand, by comparing Figs. 2a and b one can deduce that although the lowest and the highest growth rates differ by a factor of two to three this has hardly any effect on the hydrogen incorporation. The fact that the D_2 diluted plasma condition leads to a larger growth rate is due to the efficient interaction of deuterium with silane because of the slower gas phase diffusion of atomic deuterium. Furthermore, the growth rate decreases with increasing substrate temperature, which

Table II. Properties of a-Si:H deposited using the expanding thermal arc under the condition of Table I and at substrate temperature of 450 °C.

growth rate	11 nm/s	σ_{photo}	$7\times10^{-5}\ \Omega^{-1}cm^{-1}$
n_{HeNe}	4.3	$\sigma_{photo}/\sigma_{dark}$	5×10^{4}
n_{IR}	3.7	E_{act}	1 eV
[H]	4%	N_D	7×10^{15} cm^{-3}
$E_{gap,\ Tauc}$	1.69 eV	E_{Urbach}	50 meV

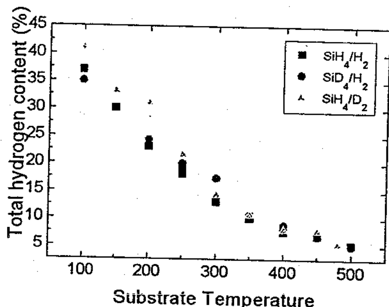

Fig. 2a. The total hydrogen (H+D) vs. substrate temperature.

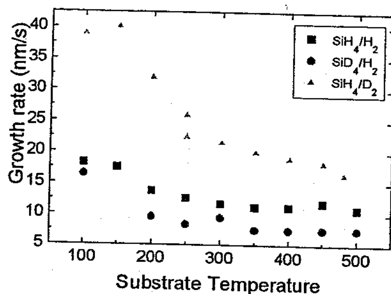

Fig. 2b. The growth rate vs. substrate temperature

is in agreement with the results of Maeda et al. [8]. In our case we could also determine the dependence of the growth flux (i.e. the actual sticking silicon atom flux) on the temperature from the ERDA results. This growth flux decreased also with increasing temperature which means that the sticking probability decreases. The results of Matsuda et al. on the other hand revealed a constant growth rate as a function of the substrate temperature [2,9]. This lead them to conclude that the sticking probability is constant, a result which can not be deduced from the growth rate only as one has to known the density of the a-Si:H grown. Moreover, Matsuda et al. reported a sharp increase of the growth rate above 350 °C, indicating the onset of hydrogen desorption from the surface [2,9]. In contrast, due to our high deposition rate, the influence of hydrogen desorption on the growth rate of a-Si:H is expected to occur at higher substrate temperatures. In other words the large supply of silyl radicals ensures the full hydrogenation of the growth surface.

Figure 3 depicts the isotope ratio (either [H]/([H]+[D]) or [D]/([H]+[D])) for the two flow conditions as a function of the substrate temperature. From the observed deuterium and hydrogen incorporation one must conclude that most of the hydrogen incorporated (about 90% for high substrate temperatures) originates from the silyl radical, about 10% originates from atomic hydrogen or deuterium. An interesting aspect of Fig. 2b is that the growth rate for flow composition 3 is about 40% smaller than for flow composition 1. Since in the former situation the surface during deposition is dominantly deuterated (more deuterium than hydrogen is incorporated), this suggests that deuterium abstraction is more difficult than hydrogen abstraction from the growth surface.

How can we explain the results of fig. 2 and 3. In a previous paper we reported an explanation for the temperature dependence of the hydrogen content. This explanation was based on an extension of the model of Matsuda, Perrin and Gallagher [6]. In this model the deposition is assumed to be governed by physisorbed SiH_3 radicals which hop over the fully hydrogenated surface. During this surface diffusion they either abstract a chemisorbed hydrogen to form silane and desorb, or they find a dangling bond and stick. Upon sticking onto a surface dangling bond, the sticked radical gains about 2 eV and becomes vibrationally excited. If just a small amount of extra energy is available, the radical can cross-link to a neighboring surface hydrogenated silicon atom, whereby a hydrogen molecule is released. This explains why so little hydrogen is

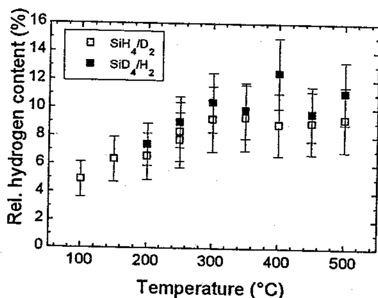

Fig. 3 The relative hydrogen (in case of SiD_4/H_2) and deuterium (in case of SiH_4/D_2) content vs. substrate temperature.

incorporated as there is just a small chemical barrier to cross-link (about 0.05-0.1 eV). A failure to complete the cross-link leads to hydrogen incorporation.

This model, which is based on the silyl radical only, would lead to a growth rate independent hydrogen incorporation (the cross-linking occurs immediately after the sticking) exactly as has been observed by Matsuda et al. [2]. On the other hand our results suggest a slight growth rate dependence. So if in our case the deposition also occurs dominantly from the silyl radical this would suggests that a time constant on the order of 30 ms (the time needed to grow one monolayer) must play a role. A possible candidate having such a timescale could be chemisorbed hydrogen diffusion. The interpretation in this case could be that a dangling bond must migrate to a site where later a chemisorbed silyl radical on this dangling bond can easily cross-link.

The model discussed would lead to the incorporation of hydrogen or deuterium attached to the silyl radical. Since we can neglect gas phase reactions which could influence the type of hydrogen isotope attached to the silyl radical, this would lead to either only hydrogen (flow composition 2) or only deuterium incorporation (flow composition 3). Since we observe the incorporation of both isotopes in both experiments we have to include the effect of atomic hydrogen or deuterium present in the plasma.

Much work has been done on the hydrogen abstraction-passivation reactions on crystalline and amorphous silicon. It is now well established that hydrogen has approximately a probability of 0.06-0.36 to abstract a hydrogen chemisorbed on a crystalline and amorphous silicon [10]. In view of these results we discuss the observations of fig. 3, noting that the hydrogen/deuterium incorporated during the growth of a-Si:H is proportional to their respective surface coverage's.

During growth the surface will be fully covered by atomic hydrogen and deuterium [11]. An important point now is that the ratio of hydrogen and deuterium on the growth surface only depends on the supply of hydrogen and deuterium (either in the form of silyl radicals or atomic hydrogen or deuterium); it does not depend on the abstraction (which is equal for both isotopes H and D) or chemisorption of a silyl radical since these processes are proportional to the surface coverage of deuterium or hydrogen and thus conserve the ratio. This inevitable leads to the conclusion that the ratio of the silyl to atomic hydrogen/deuterium flux effectively interacting with the growth surface must be similar for both situations. An important observation is the dependence of the hydrogen and deuterium incorporation on the substrate temperature. Since the incorporation depends only on the ratio of the different fluxes, we conclude that since the growth rate (and growth flux) decreases as a function of the substrate temperature less hydrogen or deuterium attached to the silyl radical is incorporated.

CONCLUSIONS

It is demonstrated that by increasing the growth rate of a-Si:H the device quality properties can still be obtained, although at a higher substrate temperature. By means of isotope labeling studies during the fast deposition of a-Si:H the hydrogen incorporation is studied. Under the conditions presented the main contributor of hydrogen in a-Si:H is the silyl radical. However, it is established that this depends solely on the relative fluxes of atomic hydrogen/deuterium and the silyl radical interaction with the growth surface.

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