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Origins of atmospheric contamination in amorphous silicon prepared by very high frequency (70 MHz) glow discharge

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The authors have studied the effect of plasma power, reactor outgassing rates, and of silane purity on the oxygen, carbon, and nitrogen contents of amorphous silicon material prepared by the very high frequency (70 MHz) glow discharge technique. The silane purity could be optionally enhanced by the application of a getter-based silane gas purifier. It was found that oxygen incorporation was enhanced at lower deposition rates, whereas the nitrogen and carbon film contamination were unaffected. The deposition rate dependence of the incorporation is in excellent agreement with a proposed model. Apart from the effects of plasma power on the incorporation probability, the reactor outgassing rate and the purity of the silane gas itself were identified as the main contamination sources for the atmospheric contaminants in the deposited films. At the low outgassing rate, at least around one-half of the oxygen detected in the *a*-Si:H material originates from the silane gas. Due to the reduced outgassing rate and an enhanced purity of the silane gas used, the authors have deposited *a*-Si:H-material with the lowest concentrations of atmospheric contaminants reported to date. Furthermore, the present results exclude a contamination of the *a*-Si:H-material by a post-oxidation after air exposure.

I. INTRODUCTION

The plasma-enhanced chemical vapor deposition (PECVD) process is the most common deposition method used to obtain device-quality hydrogenated amorphous silicon (*a*-Si:H) with a low level of atmospheric contamination. In the past, atmospheric impurities in *a*-Si:H films have been the subject of several studies. Most of them investigated the effect of these impurities on the optoelectronic properties of *a*-Si:H. It was shown in the past that atmospheric contaminants (especially nitrogen and oxygen) in the amorphous semiconductor can act as dopants[1,2] and increase the defect density when they rise above a certain concentration.[3] However, in all these studies atmospheric contaminants were intentionally added to the silane gas during the deposition and exceed the typical atmospheric contamination levels of device-quality *a*-Si:H glow discharge material (less than 5×10^{18} cm^{-3} of oxygen, 1×10^{18} cm^{-3} of carbon, and 2×10^{17} cm^{-3} of nitrogen). Due to the high oxygen content even present in device-quality *a*-Si:H, the existence of a possible relationship between the incorporated oxygen impurities and the light-induced degradation, determined by the saturated defect density of the *a*-Si:H material, remains yet an open question.[4] A reduction of the atmospheric film contaminants is, therefore, desirable and in turn requires a knowledge of the origin and quantity of the different contamination sources. Poor vacuum systems, impure gas pipes, low-quality feed gas, and post-oxidation after air exposure have all been implicated by various groups, but, to our knowledge, no systematic and quantitative study has yet been published.

Using $H_2{}^{18}O$ isotopic labeling of the adsorbed water vapor on the walls of the reaction chamber, Knights *et al.*[5] have identified outgassing as a source for the oxygen impurities in the films. Mass spectrometry shows that the residual impurities due to the outgassing of the reactor chamber basically consist of water vapor and CO. Therefore, in the absence of air leaks, the reactor outgassing and the silane gas itself, as well as the contamination by the gas line, contribute to the film contamination during the deposition. However, the quantitative contribution of all these sources on the film contamination has never been analyzed in detail and remains unclear.

Figure 1 illustrates the scenario mentioned above during the deposition. The reactor outgassing is represented by a flow $Q_{\text{outgassing}}$ of contaminants from the reactor walls in the process gas. Apart from this contamination source, the silane gas contains contaminants of a relative concentration C_{gas} (where the contribution of the pipe is included). Since $(1-C_{\text{gas}})$ is approximately 1, in the steady-state condition the total relative contaminant concentration C_{tot} of the process in the reactor can be simply expressed as the sum of each relative contaminant concentration:

$$C_{\text{tot}}=\underbrace{\frac{Q_{\text{outgassing}}}{Q_{\text{SiH}_4}}}_{C_{\text{outgassing}}}+C_{\text{gas}}, \tag{1}$$

where $Q_{\text{outgassing}}$ is the flow of contaminants, Q_{SiH_4} is the silane flow and C_{gas} the relative contaminant concentration of silane gas in the pipe.

In the absence of air leaks these two sources are responsible for the total concentration of the contaminants in the

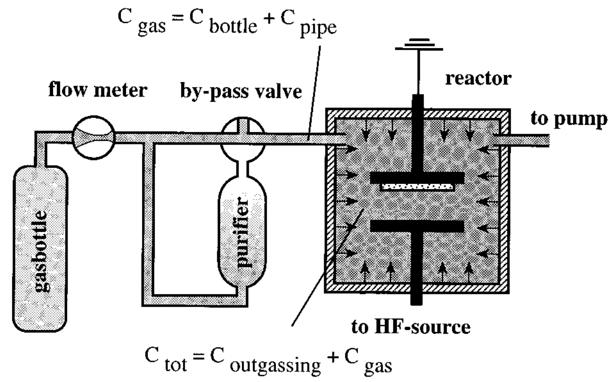

FIG. 1. Schematic representation of the deposition system used, including the commercial "Monotorr" metallic–alloy getter-based silane purifier and the sources that contaminate the process gas.

process gas. Evidently, only a certain fraction of the contaminants present in the gas phase will be incorporated in the film. Furthermore, by analyzing the impurities in the films one is only sensitive to the total concentration of the contaminants in the gas phase, i.e., to the sum of C_{gas} and $C_{\mathrm{outgassing}}$. Due to this fact, a clear separation of the main contamination sources requires independent and selective variations of C_{gas} and $C_{\mathrm{outgassing}}$. This will be achieved here by changing selectively the outgassing rate of the reactor walls and by an optional point-of-use purification of the silane gas before it enters the reactor. However, even at a constant impurity concentration in the gas phase, the incorporation probability in the film can still depend on the deposition conditions, especially on the degree of plasma excitation/ionization which, in turn, depends on plasma power.

Therefore, the purpose of this study is to demonstrate the influence of discharge power, and hence deposition rate, on the incorporation probability of contaminants from the gas phase and to identify and quantify contamination sources for atmospheric impurities in a-Si:H films. In the first part of this study, we examine the effect of the discharge power on film contamination at the constant gas phase contamination level. Then, in the second part, quantitative results will be presented to show how far the outgassing of the reactor and the silane contamination itself influence the atmospheric impurity content of a-Si:H films, as prepared by the very high frequency-glow discharge (VHF-GD) technique at 70 MHz plasma excitation frequency. We contend that our conclusions and interpretations should generally be valid for 13.56 MHz PECVD deposition systems and for other kinds of materials deposited by PECVD since, apart from the "unconventional" excitation frequency, we have used a standard capacitively coupled PECVD reactor and we do not make restrictive assumptions in our interpretation of the data.

II. EXPERIMENT

All films were deposited in a capacitively coupled parallel plate reactor (Fig. 1) using a plasma excitation frequency of 70 MHz instead of the standard industrial frequency of 13.56 MHz. Using the VHF (70 MHz) PECVD technique, an increased deposition rate, as compared to 13.56 MHz, is observed. Details are published elsewhere.[6] The depositions were performed at a pressure of 0.23 mbar, a silane flow of 40 sccm, and a temperature of 200 °C, as used by us for the deposition of device-quality material. The silane (ultrahigh purity) was obtained from Messer Griesheim (Duisburg, Germany). Atmospheric contamination in the silane gas bottle was certified at less than 5 ppm. The hf-power input was measured by a directional power meter in the 50 Ω line just in front of the matching network. The oxygen, carbon, and nitrogen contents of the films deposited on c-Si-wafers were analyzed by secondary ion mass spectroscopy (SIMS). To be sensitive to the smallest changes in the impurity levels, sandwich structures of a-Si:H layers were prepared. This means that in a single SIMS run all the different layers of the sandwich structure were analyzed under identical measuring conditions.

The SIMS measurements were carried out on a commercial CAMECA IMS $4f$ SIMS instrument using a caesium primary ion beam and negative secondary ion mass spectrometry. Concentration calibration of the oxygen, carbon, and nitrogen was achieved by using an ion implanted silicon material. The overall accuracy of the measurement and of the calibration was of the order of 15%. Instrumental backgrounds for these impurities were determined by measurement of the impurity count rates on a piece of ultrapure "float-zone" silicon. The instrumental backgrounds or the detection limits, under the chosen experimental conditions, were approximated $5\times10^{17}\ \mathrm{cm}^{-3}$ for oxygen, $5\times10^{16}\ \mathrm{cm}^{-3}$ for carbon, and $1\times10^{15}\ \mathrm{cm}^{-3}$ for nitrogen.

The outgassing of the reactor was determined by the pressure rise per time unit when the valve to the pumping unit was closed. The pressure was measured by a cold cathode gauge which was verified for reliability by a Bayard–Alpert ionization gauge. By cooling the reactor walls to room temperature, the reactor outgassing rate could be reduced from about $3\times10^{-5}\ \mathrm{mbar}\,\ell\,\mathrm{s}^{-1}$ (1.8×10^{-3} sccm) to $3\times10^{-6}\ \mathrm{mbar}\,\ell\,\mathrm{s}^{-1}$ (1.8×10^{-4} sccm). Furthermore, as shown schematically in Fig. 1, a commercial room temperature metallic–alloy getter silane gas purifier ("MonoTorr" from SAES Getters) mounted in the gas line just in front of the reactor (point-of-use) can be used in an optional mode via a bypass valve to purify the silane gas. This silane purifier with ppt (parts-per-trillion) purification efficiency[7] reduces the oxygen contamination (moisture, oxygen, and other oxygenated impurities) of the incoming silane gas in the sub-ppb range[8] by means of surface chemisorption.

The above experimental conditions were used to prepare the following samples. The first sample consists of a sandwich structure (see Fig. 2) of five layers deposited sequentially at decreasing plasma powers but identical outgassing rate; the second and third samples were deposited at different outgassing rates (see Fig. 4). Each sample in Figs. 4(a) and 4(b) consists of two layers that were deposited with and without applying the silane purifier.

Between each deposited layer in the sandwich structures the reactor was pumped to a pressure below 10^{-6} mbar.

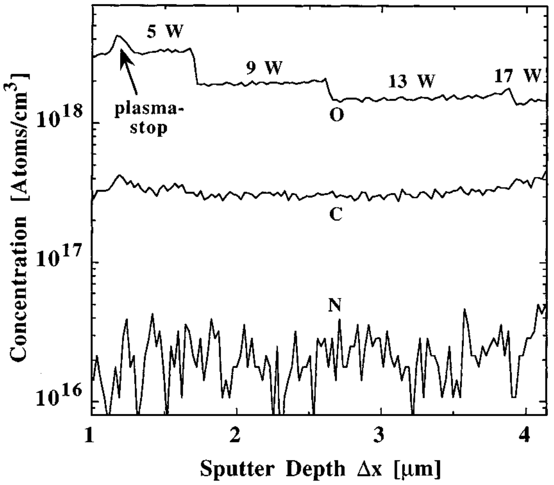

FIG. 2. SIMS profile of a sandwich structure where the layers were deposited at plasma powers of 5, 9, 13, and 17 W corresponding to deposition rates of 4.5, 9.1, 14.1, and 16.4 Å/s, respectively.

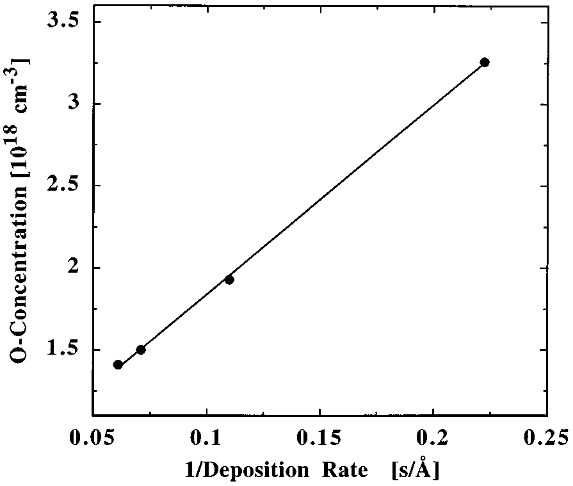

FIG. 3. Oxygen concentration of the films shown in Fig. 2 vs their corresponding reciprocal deposition rates.

III. RESULTS AND DISCUSSION

A. Variation of the discharge power

Figure 2 shows the SIMS measurement of the sandwich structure where the layers were prepared at four different hf powers. Apart from the discharge power, all other deposition conditions were kept constant. The outgassing rate, measured just before the deposition, was around 2.7×10^{-5} mbar ℓ s^{-1}, which corresponds to a flow of 1.6×10^{-3} sccm. This flow of contaminants leads to a process gas contamination of 40 ppm at the chosen silane flow. We assumed that the outgassing rate of the reactor remains unchanged during all depositions since the outgassing rate measured before and after the depositions are almost identical. Therefore a slight covering of the reactor walls by a-Si:H during the deposition does not appear to influence the reactor outgassing rate.

Although the concentration of contaminants in the gas phase is constant, the oxygen impurity level in the films is considerably reduced with increasing hf-power levels, whereas the carbon and nitrogen contamination levels remain unaffected, or at least do not show pronounced effects. It is possible that, at the lowest plasma power (5 W), a slight increase in the overall carbon level may occur; however the changes are too minor for an unequivocal statement of fact. Furthermore, a decreasing hf power induces slight reductions of the total hydrogen content in the a-Si:H layers (not shown in Fig. 2) from about 3×10^{21} to 2×10^{21} atoms/cm^3 which is, however, at such high total levels surely not related to contaminants present in the process gas.

The behavior of the oxygen demonstrates without doubt that the deposition process itself considerably influences the incorporation of oxygen. It is surprising that the O-impurity concentration does not follow the degree of ionization, i.e., the excitation of the plasma. Obviously, the decrease in oxygen content in the films is linked to the increase in deposition rate. Therefore, we suggest the following simple model for O incorporation. The contaminants present in the gas phase impinge with a certain surface collision rate on the growth zone and will be partially chemisorped or gettered there, with a certain probability p, and then buried by further deposition. Thus, as observed in Fig. 2(a), a constant flux F of contaminants will lead to a reduced incorporation in the growing layer when the deposition rate of the a-Si:H material is increased. Hence, the O concentration of the films should obey the following relationship between the surface reaction probability p, the flux F of contaminants, and the deposition rate R:

$$[\mathrm{O}] \propto \frac{p\cdot F}{R}. \tag{2}$$

In Fig. 3 the oxygen concentrations taken from Fig. 2 are plotted versus their corresponding reciprocal deposition rates. The observed excellent linear correlation is in good agreement with our proposed model, as presented in relation (2). The slope $(p\cdot F)$ of the straight line represents the flux of incorporated contaminants per area and per time unit and has a value of $p\cdot F=1.2\times10^{11}$ cm^{-2} s^{-1}.

In contrast and in comparison to the pronounced variation of the oxygen film contamination, the nitrogen and carbon levels appear to be independent of the deposition rate (see Fig. 2). As a possible explanation, we suggest that they have a lesser probability p than the oxygen contaminants to become chemisorped or gettered at the film surface during the growth, and that they are therefore preferentially incorporated in another way (e.g., via gas phase reactions with the silane and subsequent deposition of these molecules). Indeed, Tsai *et al.*[3] found from their experiments that the incorporation efficiency of oxygen is about 1000 times higher than that for nitrogen; this finding indicates a much higher reactivity of oxygen. Nevertheless, the details still remain unclear. Additional evidence of the high reactivity of oxygen contaminants will be discussed.

During the 5 W layer deposition the discharge was accidentally extinguished. After around 1 min the plasma was reignited and deposition was continued. As a result of this "plasma stop," a definite kink in the oxygen content and

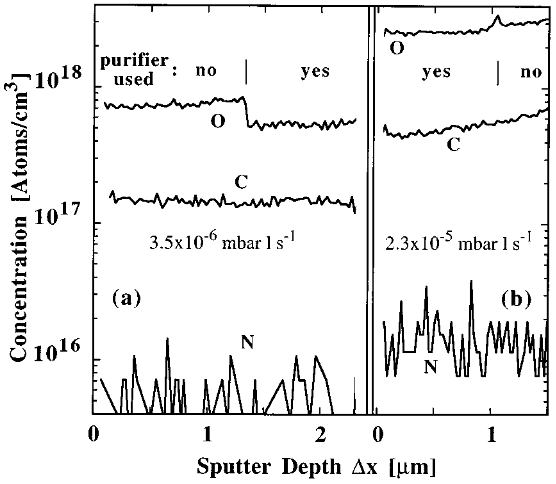

FIG. 4. SIMS profiles of two sandwich structure samples. The sandwich layers were deposited with and without applying the silane purifier at a discharge power of 9 W. The difference between (a) and (b) is the outgassing rate of the reactor.

possibly a small kink in the carbon content are observed in the SIMS spectrum. This indicates that, even in the absence of a plasma, the growth surface seems to be capable of reacting with the oxygen contaminants present in the gas phase which are basically composed of water vapor from the outgassing and maybe even with the carbon contaminants, but much less effectively.

Identical observations to the oxygen incorporation behavior presented here have already been observed[9] for intentionally added dopants in the gas phase where incorporation was found to be more efficient in *a*-Si:H films deposited at lower deposition rates, i.e., at lower discharge power. Therefore, our simple model discussed above seems to be valid also for gas phase doping and offers a supplementary explanation to a phenomenon that is still not fully understood.[9]

B. Influence of the outgassing rate and the application of the silane purifier

In these experiments, the deposition rate was kept constant and the concentration of the contaminants in the gas phase was varied by varying the outgassing and by application of the gas purifier, which reduces or even removes oxygen contaminants in the silane flowing in the reactor. The outgassing rate could be reduced by cooling the reactor walls to room temperature. The manner in which the atmospheric impurity concentrations in the deposited films depend on these two sources is shown in Fig. 4. The two different outgassing rates are indicated in Figs. 4(a) and 4(b). In Fig. 4(b), the difference caused in the oxygen levels of the films by application of the purifier is less pronounced than in Fig. 4(a), where the outgassing rate was lower. According to Eq. (1), it seems that for Fig. 4(b) the oxygen contamination arising from an outgassing of 2.3×10^{-5} mbar ℓ s^{-1} (this leads to 35 ppm of contaminants in the silane gas at a flow of 40 sccm) overlaps and even almost completely masks the contamination of the incoming gas and thus represents the main contamination source. Unaffected by the application of the silane purifier, the carbon and nitrogen concentrations remain at 5×10^{17} and 1×10^{16} cm^{-3}, respectively.

By a reduction of the outgassing rate to 3.5×10^{-6} mbar ℓ s^{-1} [this leads to 5 ppm of contaminants in the silane gas at a flow of 40 sccm in Fig. 4(a)], all three atmospheric contaminants in the film (O, N, and C) decrease at least by half an order of magnitude and are reduced (at least partly) to values very close to the SIMS detection limit. This large reduction confirms that outgassing plays an important role in film contamination and does indeed represent a major source of contamination.

Furthermore, since strong changes of the impurity levels are observed, we can now discard the hypothesis that diffusion of atmospheric impurities in the film after air exposure contributes significantly to film contamination. At this smaller outgassing rate, the application of the silane purifier reduces the oxygen concentration further, as can be seen in Fig. 4(a), from the pronounced step in the SIMS profile. This illustrates the fact that now both the contribution of the outgassing rate and the purity of the silane gas present in the pipe, to the oxygen impurity level of the films, reach a comparable magnitude and, thus, now represent the major sources of contamination. In addition, when the purifier was used, the detected oxygen contamination in the films was very close to the SIMS detection limit and it may be possible that the true concentration is even lower.

An estimate of the contribution of gas contamination to film impurity can be obtained by the difference in the two oxygen concentrations measured with and without applying the silane purifier [see Fig. 4(a)]. Consequently, in our deposition process, and under the above mentioned conditions, at least 3.0×10^{17} oxygen atoms per cm^3 in the *a*-Si:H films arise from silane gas contamination already present in the pipes. We suspect that, even after a good purging and pumping of the gas pipe, a substantial portion of the atmospheric contaminants in the silane gas entering the reactor originally comes from the gas pipe. However, strong evidence cannot be presented yet and it requires further investigations.

Therefore, even at a negligible outgassing rate (in the ideal case it equals zero), at least the above-mentioned contribution to oxygen contamination will always be present if no purifier is used and causes a lower limit of contamination in the films. If, furthermore, we also take into account the influence of the deposition rate, it is evident that this level will move upward at lower deposition rates.

Conversely, an oxygen film contamination of at most 5×10^{17} cm^{-3}, as shown in Fig. 4(a), originates solely from the present reactor outgassing of 3.5×10^{-6} mbar ℓ s^{-1} since, in this case, the gas purifier was applied.

In summary, the results found above clearly demonstrate that the outgassing rate and the silane gas contamination are directly correlated to film contamination levels obtained and that they represent the main sources of contamination in the PECVD process. Using our fast deposition rate, the application of the silane purifier, and a reduced outgassing rate, we were able to deposit the purest *a*-Si:H material reported to date. This *a*-Si:H material contains the following atmospheric impurity concentrations: [O]: 5×10^{17} cm^{-3}, [C]: 1.5×10^{17} cm^{-3}, and [N]: less than 1×10^{16} cm^{-3}. Note that the true concentrations of these elements may be even lower since the detected levels are close to the SIMS detection limit.

IV. CONCLUSIONS

In conclusion, we have identified that the outgassing rate and the gas contamination present in the pipe are the main sources for the atmospheric contaminants found in *a*-Si:H films. At a high outgassing rate, the outgassing of the reactor is almost entirely responsible for the atmospheric impurities in the films and masks the contribution of silane contamination already present in the pipes. When the outgassing rate is reduced, the contaminants introduced by the silane gas itself become more and more dominant. Due to the application of a metallic–alloy getter-based silane purifier that efficiently removes the oxygen contaminants present in the silane gas, we could determine that at the lower outgassing rate of 3.5×10^{-6} mbar ℓ s^{-1} at least 40% of the oxygen contaminants incorporated in the *a*-Si:H material were originally from the silane gas. Under these deposition conditions the silane gas contamination c_{gas} is responsible for an oxygen film contamination of at least 3.0×10^{17} cm^{-3}.

Since the film contamination of the *a*-Si:H material deposited here depends strongly on the above-mentioned sources of contamination, a significant indiffusion of atmospheric contaminants after air exposure does not appear; therefore this mechanism can be rejected as a film contamination source of practical importance.

Independent of the contaminant concentration in the gas phase, an increased deposition rate also clearly reduces the incorporation of the oxygen in the films. Our proposed model of contaminant incorporation in the growing films is in excellent agreement with this observed behavior. Therefore, the VHF process, due to its enhanced deposition rate,[6] is more compatible with the deposition of pure material than PECVD deposition at the standard industrial frequency of 13.56 MHz.

After considering all the above findings and by using the silane purifier, we are able to deposit the purest *a*-Si:H material reported up to now with $[\mathrm{O}]\leqslant5\times10^{17}$ cm^{-3}, $[\mathrm{C}]=1.5\times10^{17}$ cm^{-3}, and $[\mathrm{N}]\leqslant1\times10^{16}$ cm^{-3}.

Since we do not make any restrictive assumptions in our discussion, we hold that our conclusions and interpretations should still be valid in most other PECVD deposition systems used for *a*-Si:H and even for the plasma-assisted deposition of other kinds of materials.

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