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ANALYSIS OF CVD BY SURFACE ANALYSIS TECHNIQUES AND IN-SITU MASS SPECTROMETRY

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Abstract – The reaction between WF_6 and Si has been studied with a specially designed mass spectrometer set-up, and by AES depth profiling. The time development of the reaction is monitored via the reaction product SiF_4 . Two stages can be distinguished. The first stage is a quick rise to a maximum SiF_4 signal. During this stage most of the F is absorbed in the Si, forming a reaction layer of SiF_n moieties. The tungsten covers the surface in an open structure. In the second stage, these SiF_n moieties desorb after the addition of the necessary F atoms, supplied by adsorbing WF_6 . The total amount of SiF_n moieties decays exponentially with time. The rate limiting step is the formation of SiF_4 with an activation energy of 1.6 ± 0.2 eV, probably the addition of F to SiF_3 .

1 Introduction

In situ mass spectrometry is a powerful technique in the analysis of CVD processes. Simply coupling a mass spectrometer to a CVD-reactor, however, hardly ever creates a situation suited for studying the desired reaction. Because of poorly defined gas flow conditions, the time resolution of the analysis will also generally be poor. Also products, formed after the actual deposition reaction, may be observed. We have largely circumvented these problems in our specially designed mass spectrometer set-up.

With this set-up we have investigated the W-CVD process, based on WF_6 , with the overall reaction

The deposited W layer will cover the underlying Si. Therefore the reaction will stop after a certain layer thickness is reached. Two conflicting reports have been made on the temperature behaviour of the limiting W layer thickness. The difference in observation seems to be caused by the kind of reactor used. Depositions in hot wall reactors result in temperature independent layers with a thickness of 15-20 nm [1, 2]. Cold wall reactors, on the contrary, show an Arrhenius type temperature behaviour of the layer thickness, with an activation energy of 0.33 to 0.48 eV [3, 4]. The thicknesses then found, range from 5 to 500 nm at temperatures of 400 to 800 K.

Also reports on hot wall reactors have been made of temperature dependent layer thicknesses, with a maximum of about 100 nm at 600 K [5]. It has been shown however that this behaviour is caused by poor surface conditions [1, 2]. In this report, we present time resolved mass spectrometer

Figure 1: The mass spectrometer set-up schematic. The reactor is formed by a quartz tube. Gaseous reactants and products can enter the mass spectrometer compartment through a pinhole in the reactor wall. The ionization chamber of the mass spectrometer is surrounded by cryoshields to prevent the detection of molecules which have probably reacted inside the mass spectrometer compartment.

measurements and additional AES depth profiles, which give new insights into the growth and the nature of the limiting character of the WF_6/Si process.

2 Experimental

The mass spectrometer set-up is shown in Figure 1. The reactor is formed by a quartz tube. Reactor tubes are cleaned after each deposition. Care has been taken to minimize the H_2O concentration in the reactor. For this purpose, the reactor tubes are baked out for at least 15 hours at 1000 K, while a low pressure Ar flow (99.999%) is supplied to the tube.

The 5×9 mm sample, cut out of a 4 inch Si (100) wafer, is cleaned by an HF etch procedure prior to introducing it into the reactor. The sample can be heated by a tube heater, placed around the reactor. In a separate experiment it has been shown that the sample temperature and heater temperature are equal within 1 K. A room temperature gas flow (10 sccm, 10 Pa) did not change the temperature within experimental error.

The gases WF_6 and Ar can be supplied to the reactor or a by-pass. By means of a cross valve, the two independent gas flows can be changed from one to the other.

At 1 mm from the end of the reactor tube, a quartz plate is placed with a pinhole in its center. The main gas flow is pumped away through the space between the reactor tube and the quartz plate. A fraction of the gas molecules, however, will flow through the pinhole into the mass spectrometer compartment. The incoming molecules are detected by a quadrupole mass spectrometer. The ionization chamber of the mass spectrometer is surrounded by cryoshields at 20 K. Only molecules which travel in a straight line from the pinhole to the ionization chamber will be detected. In this way, the time resolution is preserved. Furthermore, the detection of molecules

Figure 2: Typical time resolved mass spectrometer measurement, with $\bullet$ = SiF_4 , $\circ$ = WF_6 and $+$ = WOF_4 . At $t = 10$ s WF_6 is supplied to the reactor. The measure time per data point is 100 ms.

which have possibly reacted with the wall or with other molecules within the mass spectrometer compartment, is prevented. The typical pressure in the mass spectrometer compartment under experimental conditions is 7×10^{-7} Pa.

Depositions are performed as a function of both the exposure time of WF_6 and the temperature. Before WF_6 is supplied to the reactor, the reactor is evacuated and no gas is supplied to the reactor. During this time the sample is heated to the desired temperature and a WF_6 flow (0.2 sccm) is established in the by-pass. At a certain time the WF_6 flow is switched to the reactor, causing the pressure in the reactor to increase to 20 Pa and the deposition to start. During the deposition an Ar flow (3 sccm) is established in the by-pass. When the desired exposure time is reached, the WF_6 flow and the Ar flow are swapped. At the same time the heater is turned off.

As a function of time, the signals of SiF_3^+ , WOF_3^+ and WF_5^+ resulting from SiF_4 , WOF_4 and WF_6 respectively, are measured. WOF_4 is an indicator for H_2O , as it is a reaction product of the reaction between WF_6 and H_2O . Measurements with a significant WOF_4 signal are rejected.

After cooling down, the samples are analyzed by AES, combined with 4 keV Ar^+ sputtering.

3 Results

A typical time resolved mass spectrometer measurement is shown in Figure 2. At $t = 10$ s, WF_6 is supplied to the reactor. At the same time the SiF_4 signal increases, showing the reaction takes place. After some time, SiF_4 has reached a maximum, and an exponential decay follows. As can be seen from Figure 2, the exponential behaviour is observed over as much as 3 decades. The slope of the decay, ν , is temperature dependent, i.e. a higher temperature results in a steeper slope.

The area beneath the SiF_4 curve is proportional to the amount of Si consumed. This area appears to be independent of temperature, so the limiting W layer thickness is independent of temperature too [6]. From the exponential decay it follows that the total amount of Si that will

Figure 3: Arrhenius plot of ν_{SiF_4} . The solid line is a least square fit of $\nu = \nu_0 \exp E_a/kT$, with $\nu_0 = 10^{13} \text{ s}^{-1}$, using the data points at temperatures less than 570 K. This yields $E_a = 1.6 \pm 0.2 \text{ eV}$.

be consumed is determined when the exponential decay is started.

The decay constant found, ν_{SiF_4} , is to be interpreted as the reaction rate constant for the production of SiF_4 since

$$\frac{d\text{SiF}_4}{dt} = -\nu_{\text{SiF}_4} \text{SiF}_4. \quad (2)$$

The SiF_4 production is an energy activated process, as can be seen from the Arrhenius plot of ν_{SiF_4} in Figure 3. A least square fit of the points at temperatures less than 570 K, with a pre-exponential factor $\nu_0 = 10^{13} \text{ s}^{-1}$, yields an activation energy of $1.6 \pm 0.2 \text{ eV}$. Above 570 K, the slope is less steep. This might indicate that another process, probably a transport controlled mechanism, becomes rate limiting. It is also possible that the fast decay is limited by experimental conditions.

When the WF_6 supply is terminated, while the SiF_4 signal is decreasing, an extra amount of desorbing SiF_4 is observed. It is not possible to quantify this extra amount, because at the same time the pressure in the reactor decreases due to the termination of the WF_6 flow. Again supplying the WF_6 restores the SiF_4 signal after which the earlier exponential decay continues.

Stopping and re-starting the WF_6 flow after the SiF_4 signal has become zero, does not result in a new SiF_4 signal. The W layer thus has covered the Si completely.

The AES depth profiles are taken after depositions at the temperatures 500 K, 540 K, 570 K and 650 K. At each temperature, the WF_6 exposure time was varied. A typical result for the Si and W depth profile at different exposure times is shown in Figure 4. From the depth profiles it follows that the Si concentration is practically constant in the outer layers. As the WF_6 exposure time increases, the Si concentration in the outer layers decreases. At very long exposure times, the Si concentration reaches zero in the outermost layers, as is also found by Kuiper et al. [4]. The Si concentration does not drop to zero in the subsurface layers during the deposition. This rules out models of the layer growth, which require Si transport along pores or grain boundaries of a complete tungsten layer.

Figure 4: AES depth profiles of W layers on Si, grown at 540 K at different exposure times of WF_6 . The sputter rate is estimated to be 2 nm min^{-1} .

At the surface of the samples, 20 % of a monolayer of O is found, which most probably is formed during transport from the reactor to the AES apparatus. The amount of O within the layers was less than the detection limit. In contrast, analysis of a rejected sample (rejected on base of a WOF_4 signal), did show an O content of 8% at the depth where the original Si surface should have been.

The F concentration in the sample is expected to be low, because during cooling down the sample, and transport to the AES apparatus, the remaining F will react with air or desorb as SiF_4 . This is also indicated by the observation of the extra amount of SiF_4 desorbing after terminating the WF_6 flow. Indeed no F was detected, but this might also be caused by electron beam induced removal of F during the AES analysis.

The depth profiles at large WF_6 exposures are equal, within experimental error, for the four different temperatures. This indicates that the layer thickness is independent of temperature.

When the Si concentrations in the outer layer are plotted versus the exposure time, the Si concentration in the outer layers decays exponential with time, at the same rate as the SiF_4 desorption signal does as can be seen from Figure 5 for $T = 575 \text{ K}$. This correlation also holds for the other temperatures.

An Arrhenius plot of the decay constant is shown in Figure 6. The point at 650 K was estimated to be a lower limit for ν_{Si} at that temperature. A least square fit of the other data points, with a pre-exponential factor $\nu_0 = 10^{13}$ yields an activation energy of $1.57 \pm 0.05 \text{ eV}$. Although the data points are few, the good agreement with the time resolved mass spectrometer results justifies the procedure followed.

4 Discussion

In our previous work, the time resolved mass spectrometer measurements has been discussed [6]. The main conclusions will be briefly summarized.

The SiF_4 signal, found in the time resolved mass spectrometer measurements, is in fact the desorption rate of SiF_4 . This desorption is a final result of many sequential steps, one of them being rate limiting. In the etching of Si by XeF_2 , it is observed that F atoms not only adsorb on the surface, but also penetrate the underlying layers. In this way a kind of reaction layer,

Figure 5: SiF₄ signal (solid line) and Si concentration in the outer layers (•) versus WF₆ exposure time.

consisting of SiF_n moieties is formed [7].

Two stages are distinguished in the deposition process. The first is the build-up of the reaction layer, in which the SiF₄ desorption increases to a maximum. The build-up of the reaction layer is terminated in some way. With this termination, the total amount of Si that will be consumed is determined. The second stage is the desorption of the determined amount of Si as SiF₄. This is observed by the exponential decay of the SiF₄ signal.

The rate limiting step is assumed to be the addition of a F atom to a SiF_n moiety at the surface. The change of the concentration of SiF_n at the surface, [SiF_n], is described by

$$\frac{d[\text{SiF}_n]}{dt} = -j_{\text{decr}} + j_{\text{incr}}, \quad (3)$$

where j_{decr} represents the decrease due to the reaction with F and j_{incr} takes into account the Si supply from bulk to surface. Since the amount of Si, involved in the exponential decay, is more than one monolayer, equation 3 must also hold for the SiF_m concentration in the reaction layer, [SiF_m]. This implies that, apart from a constant, [SiF_n] can be replaced by [SiF_m] and that j_{incr} vanishes. The assumption that [SiF_n] and [SiF_m] are in thermal equilibrium fulfils this requirement. The influence of the WF₆ density is the disturbance of the equilibrium.

From the AES depth profiles, it follows that the SiF_m concentration at the surface is proportional to the SiF₄ production during the tungsten deposition as has been demonstrated in Figure 5. The gradient of the Si concentration in the outermost layers is small, which supports the assumption of the thermal equilibrium between [SiF_n] and [SiF_m].

The high Si concentration in the outer layers conflicts with a model in which Si diffuses to the surface along grain boundaries. Furthermore, from the time resolved mass spectrometer analysis it follows that in the first stage of the desorption nearly the total amount of Si, which will be consumed in the deposition, is stored. In the second stage of the deposition this stored amount is used up. Therefore it must be concluded that the Si is supplied from a reaction layer, which is controlled by the reactions at the surface.

Figure 6: Arrhenius plot of ν_{Si} . The solid line is a least square fit of $\nu = \nu_0 \exp E_a/kT$, with $\nu_0 = 10^{13} \text{ s}^{-1}$. This yields $E_a = 1.57 \pm 0.05 \text{ eV}$.

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