Silicon nitride films deposited from SiF_4/NH_3 gas mixtures

C. GOMEZ-ALEIXANDRE, O. SANCHEZ-GARRIDO, J. M. MARTINEZ-DUART, J. M. ALBELLA
Institut Ciencia de Materiales, CSIC, Universidad Autonoma, C-12 Cantoblanco 28049 Madrid, Spain

Silicon nitride films have been deposited from $SiF_4/NH_3/H_2$ gas mixtures. The deposition reaction at high pressure (52 torr), takes place only for temperatures above 800 °C. In the temperature range 800–1 000 °C the reaction is controlled by a surface process. The increase in H_2 and SiF_4 partial pressures enhances the deposition rate. The SiF_4 molecules provide a high concentration of available silicon atoms, while the hydrogen molecules inhibit the etching effect of the free fluorine atoms. Finally, the effect of an r.f. plasma in the chemical vapour deposition reaction has been evaluated.

1. Introduction

Silicon nitride films have been extensively investigated for applications in semiconductor devices and in ceramic coatings. The films are usually obtained by chemical vapour deposition (CVD) techniques from different silicon precursors, such as SiH_4, $SiCl_2H_2$, $SiCl_4$ or SiF_4. Among them, silane (SiH_4) has been the most widely studied. However, silicon nitride films deposited from silane show large numbers of hydrogen radicals incorporated in their structure [1, 2]. The –SiH radicals formed from the hydrogen atoms incorporated in the network may act as charge traps in the silicon nitride [3, 4] and produce a great instability in the electric characteristics of the devices [1]. In this regard, some attempts have been made to reduce the presence of these radicals. When a fluorine source is present, it seems that the fluorine atoms are able to substitute the hydrogen atoms linked to silicon atoms, resulting in Si–F bonds with a bonding energy (128.4 kcal mol^{-1}) much greater than the Si–H bonding energy (70.4 kcal mol^{-1}) [5]. Furthermore, it has been shown that fluorine atoms saturate the extra silicon dangling bonds in the film, thus preventing the formation of traps in the nitride and also producing a decrease in the surface state density.

However, when SiF_4 is used as reactant gas, a large decrease in the stability of silicon nitride films in oxygen atmospheres has been detected. Fujita *et al.* [5, 6] deposited silicon nitride films from $SiF_4/N_2/H_2$ gas mixtures at 350 °C in an r.f. plasma. They observed atoms of oxygen incorporated in the Si–N network which Chang *et al.* [4] interpreted as due to the subsequent oxidation of the film, induced by the presence of fluorine atoms. Owing to the low deposition rate of the fluorinated silicon nitride films deposited by this method, Fujita *et al.* tried to enhance the process by a previous reduction of the SiF_4 molecules to the more active SiF_2. On the other hand, it is expected that the substitution of nitrogen by ammonia in the gas mixture should improve the kinetics of the reaction, because the NH_3 bonding energy (104 kcal mol^{-1}) is much lower than the N_2 bonding energy (226 kcal mol^{-1}). In addition, the reactions using NH_3 are thermochemically more favourable than similar reactions using nitrogen, because of the higher free energy of formation of ammonia [7].

Although some authors have obtained pyrolytic silicon nitride by CVD from SiF_4 and NH_3 [8–10], the reaction is still not well investigated. It is known, that the CVD reaction can be enhanced by using an r.f. discharge as has been widely pointed out [11, 12], thus allowing a reduction in the deposition temperature from that normally needed to decompose the SiF_4 molecules (above $\simeq$ 800 °C). In the present work, we have studied the kinetics of the $SiF_4 + NH_3$ reaction for silion nitride deposition in a CVD system at low pressure. The effect of the deposition parameters (temperature, gas flow rate, etc.) has been investigated. In addition, the influence of an r.f. plasma applied on the reactor in a remote configuration was also evaluated.

2. Experimental procedure

The deposition system consists of a quartz tubular hot-wall reactor of about 100 cm long and 6 cm diameter. The total pressure in the reactor was kept constant by a controlled butterfly valve, located just before the vacuum pump. The silicon nitride was deposited from $SiF_4/NH_3/H_2$ gas mixtures. The SiF_4 flow rate was varied between 30 and 192 standard $cm^3\ min^{-1}$ (sccm) and the $[H_2]/[SiF_4]$ flow ratio was kept in the range 0–20. The NH_3 flow rate was approximately 20%–40% total gas stream, its value being always higher than the SiF_4 flow rate. The H_2 and NH_3 gas mixture was introduced in the reactor separated from the SiF_4, because NH_3 and SiF_4 can react at room temperature resulting in a solid compound which clogs the gas lines (see below). For this

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reason, the SiF_4 gas was injected directly into the reaction zone. The r.f. plasma (13.56 MHz) was inductively coupled either downstream or upstream in order to determine the influence on the reaction rate.

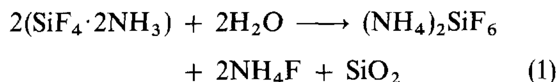
The silicon nitride films were deposited on to (1 1 1) p-silicon substrates polished on both sides. Analysis of the films were performed by infrared spectroscopy (Hitachi model 270–50). Only the absorption peak corresponding to the Si–N bond ($860\ cm^{-1}$) was detected in the infrared spectra. This indicates that other radicals typically observed in low-temperature deposition (–NH, –SiH, etc.) were under the detection limit. The thickness of the films was determined by ellipsometry (Gaertner, L116).

3. Results and discussion

3.1. Low-temperature reaction of SiF_4 and NH_3

As mentioned above, the SiF_4 and NH_3 can react spontaneously at room temperature producing a hard crystalline material of whitish colour, identified by X-ray analysis as a mixture of $SiF_4{\cdot}2NH_3$ and $(NH_4)_2SiF_6$ [13]. Fig. 1 presents the X-ray diffraction spectrum of this material, where the peaks corresponding to the last compound, $(NH_4)SiF_6$, are marked with an arrow. An increase in the NH_3 flow rate produces a displacement of the reaction, increasing the formation rate of fluor-nitro compounds.

The adduct compound, $SiF_4{\cdot}2NH_3$, is a typical product in the addition reaction of SiF_4 and NH_3 [14]. This compound is able to hydrolyse according to the reaction



$$2(SiF_4{\cdot}2NH_3) + 2H_2O \longrightarrow (NH_4)_2SiF_6 + 2NH_4F + SiO_2 \qquad (1)$$

Therefore, the $(NH_4)_2SiF_6$ can be formed by the reaction of the previously formed adduct compound during the deposition process with moisture when the samples are exposed to the air atmosphere.

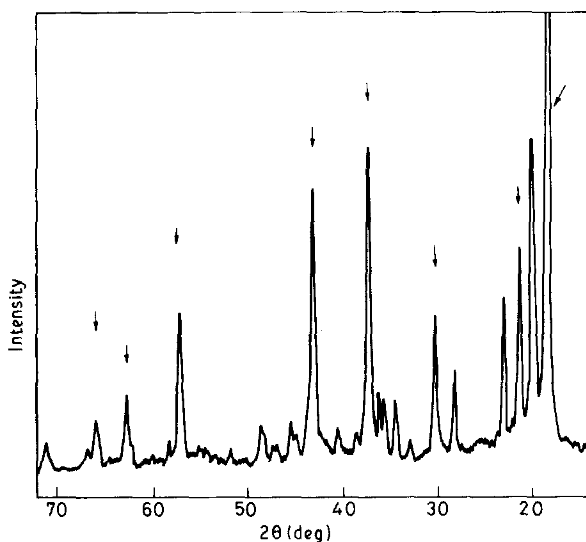
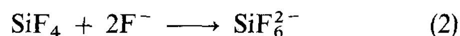


Figure 1 X-ray diffraction spectrum corresponding to the crystalline material obtained in the low-temperature reaction of the SiF_4 and NH_3 gases.

In addition, the SiF_4 molecule could react with more fluorine ions forming hexafluorsilicate complexes such as $(SiF_6)^{2-}$ according to the reaction [14]



$$SiF_4 + 2F^- \longrightarrow SiF_6^{2-} \qquad (2)$$

However, this reaction is scarcely probable, because at this low temperature the concentration of free fluorine in the reaction chamber is very low.

For temperatures above 100 °C no hard deposits were detected in the reactor, probably due to the low sublimation temperature of the adduct compound 75–115 °C [13].

3.2. Effect of temperature on the $SiF_4 + NH_3$ reaction

The effect of temperature on the kinetics of formation of the silicon nitride films was first investigated. The films were deposited from $SiF_4/NH_3/H_2$ gas mixtures using $[NH_3]/[SiF_4] = 5$ and $[H_2]/[SiF_4] = 20$ gas ratios, with a total flow rate of 2.5 standard litres min^{-1}, and a total pressure of 52 torr (1 torr = 1.333×10^2 Pa). The deposition process was carried out directly, feeding the SiF_4 gas into the reaction region, in order to avoid the adduct formation in the cold zones of the reactor tube. The substrates were placed about 10 cm away from the SiF_4 gas inlet where the highest amounts of deposit were found to occur.

The deposition of silicon nitride started at temperatures higher than about 800 °C. This fact can be attributed to the elevated bonding energy of the SiF_4 molecule (144 $kcal\ mol^{-1}$). As can be seen in Fig. 2, the film thickness increases as the temperature varies from 900–1000 °C. For this temperature range, the activation energy calculated from an Arrhenius plot is 35.9 $kcal\ mol^{-1}\ grad^{-1}$, which can be associated with a reaction controlled by a surface process [11, 15].

In Fig. 2, the Arrhenius plot using silane, i.e. $SiH_4/NH_3/N_2$ gas mixtures, is also presented [15]. In this deposition process, the gas flow rates were: $[SiH_4] = 1.4$ sccm, $[NH_3] = 25$ sccm and $[N_2] = 139$ sccm. Both Arrhenius plots show similar activation energies, so the same controlling steps in the reactions can be assumed. It is worth mentioning that the similar deposition rates observed, even though the SiF_4 flow rate is 70 times higher than the SiH_4 flow rate, prove that the reactivity of the SiF_4 molecule is much lower than that of SiH_4.

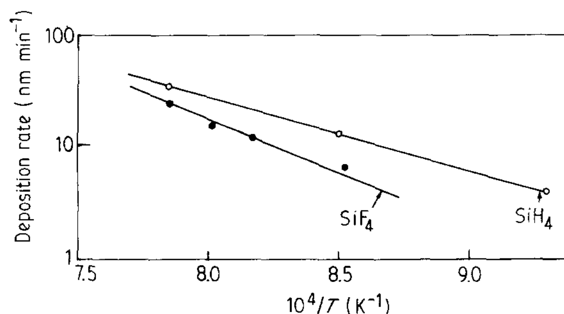


Figure 2 Arrhenius plot for the reaction of SiF_4 and NH_3 gas mixtures.

3.3. Effect of addition of hydrogen

The dissociation energy value of the SiF_4 molecule (589.7 kcal mol^{-1}) explains the higher stability of the SiF_4 molecule with respect to other gaseous silicon sources [16]. At elevated temperatures, SiF_4 present as a reactant gas produces a high concentration of fluorine atoms in the reaction chamber. These atoms etch the silicon substrate as well as the deposited silicon nitride [4, 17]. The concentration of free fluorine in the gas phase can be decreased by the addition of a source of hydrogen (such as H_2 or SiH_4) [5]. For this reason, we have studied the influence of hydrogen added to the reactant gases. In this case, the samples were deposited from $SiF_4/NH_3/H_2/N_2$ gas mixtures (100:730:0–2000:2000–0)at 1000 °C and at a constant pressure of 10 torr. Fig. 3 shows the effect of the addition of hydrogen on the deposition rate of silicon nitride. As can be observed, the presence of hydrogen in the gas mixture enhances the deposition reaction. The increase in the deposition rate with the hydrogen concentration in the gas mixture agrees with the results of Fujita *et al.* and can be explained by a reduction in the etching effect of SiF_4 on the growing surface [5, 18]. Interestingly, in some experiments, a reduction in the deposition rate with time was observed, which indicates that an inhibition mechanism of the reaction takes over during the process. This effect can be due to an increase of fluorine atoms on the surface with the deposition time, producing a progressive passivation which prevents the growth process.

3.4. Effect of SiF_4 partial pressure

The SiF_4 flow rate was varied between 30 and 150 sccm whereas the total flow rate was kept constant by the corresponding reduction in the hydrogen flow rate. In this series of experiments the following conditions were used: SiF_4 flow rate 30, 90, 120, 150 sccm; H_2 flow rate 1000, 940, 910, 880 sccm; NH_3 flow rate 730 sccm; pressure 7 torr; temperature 1000 °C.

As can be observed in Fig. 4, the deposition rate increases linearly when the SiF_4 partial pressure increases between 100 and 600 mtorr. The linear relation between the deposition rate and the SiF_4 partial pressure observed in this set of experiments can be explained by a displacement of the equilibrium reaction to the Si_3N_4 formation when the concentration of any of the reactant gases increases. Similar results have been reported by Yi *et al.* [19] and Grieco *et al.* [20] when $SiCl_4$ and NH_3 are used for the deposition of silicon nitride films. As has been mentioned in Section 3.3, the decrease in the $[H_2]/[SiF_4]$ gas ratio produces a reduction in the deposition rate. Therefore, the effect of SiF_4 partial pressure on the deposition rate can be stronger than the results shown in Fig. 4, where a simultaneous decrease in the $[H_2]/[SiF_4]$ ratio occurs.

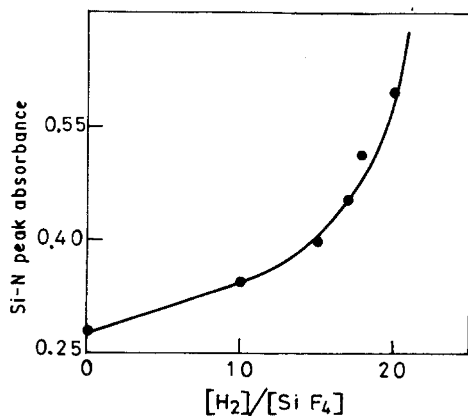


Figure 3 Deposition rate versus $[H_2]/[SiF_4]$ gas ratio in the silicon nitride deposition from $SiF_4/NH_3/H_2/N_2$ gas mixtures.

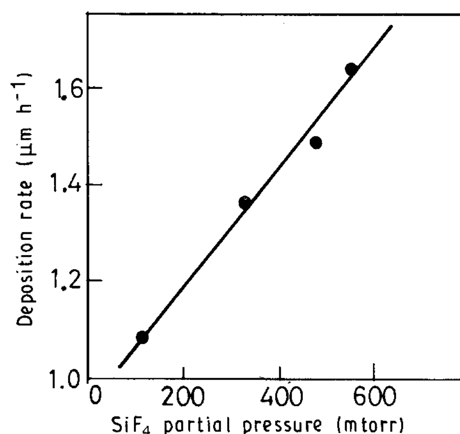


Figure 4 Variation of the deposition rate of silicon nitride with the SiF_4 partial pressure.

3.5. Effect of r.f. plasma

As is known, the presence of an r.f. plasma produces an enhancement in the CVD reaction process due to the extra activation of gas species in the plasma [11]. In this work, the r.f. plasma has been inductively coupled in the external part of the reactor tube (remote plasma configuration). Therefore, the gas species are activated before they reach the hot zone of the reactor, where the surface reaction takes place. The distance between the induction coil and the substrate has a major effect on the deposition rate. Fig. 5 shows a lesser effect of the plasma on the reaction rate when the substrate–induction coil distance increases. This effect has also been observed for different r.f. powers within the 0–400 W range. It can be attributed to the deactivation of excited species by collisions along the path inside the reactor tube.

The effect of the r.f. power on the film thickness has been studied in samples located in the middle of the furnace, separated 39 cm from the coil. Fig. 6 shows a linear increase in the thickness with the r.f. power for a constant deposition time of 60 min. This variation, also observed by other authors [21–23], has been explained by the increase in the electron temperature when the r.f. power becomes higher [21]. On increasing the electron temperature, the dissociation rate of those gas species having a greater dissociation energy increases, giving rise to a larger concentration of corresponding free radicals. Because the bond energy of the SiF_4 molecule (144 kcal mol^{-1}) is much greater than that of the NH_3 molecule (104 kcal mol^{-1}) [24],

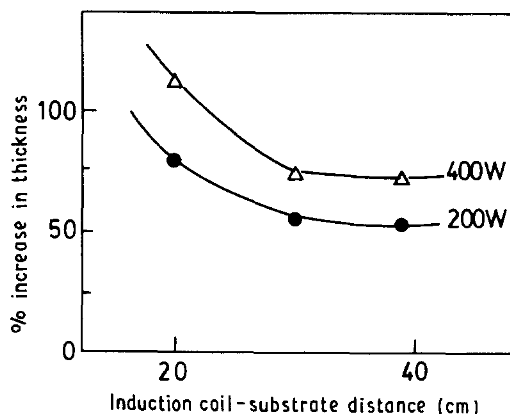


Figure 5 Effect of the plasma on the reaction rate when the substrate–induction coil distance is varied.

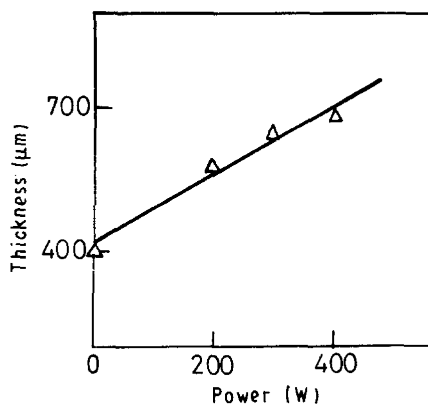


Figure 6 Variation of the silicon nitride thickness with the r.f. power.

one can expect an increase in the silicon-containing radicals inside the plasma when the r.f. power becomes higher. In this way, in our experiments, always performed in an excess of ammonia, the increase in the r.f. power will improve the deposition rate of silicon nitride.

4. Conclusion

CVD and PECVD silicon nitride films have been deposited from $SiF_4/NH_3/H_2$ gas mixtures. The deposition reaction at high total pressure (52 torr) takes place only for temperatures above 800 °C. The process is controlled by a surface reaction in the temperature range 800–1000 °C. In addition, it has been found that SiF_4 gas feeding should be introduced separately from the $NH_3 + H_2$ gas lines. The inlet must also be directly placed in the reaction zone, in order to avoid adduct formation ($SiF_4 \cdot 2NH_3$) in the cold regions of the reactor.

The addition of hydrogen to the gas mixture produces an enhancement in the deposition rate, probably by the inhibition of the etching effect of fluorine atoms on the deposited films. When the NH_3 is in excess in the gas mixture, the reaction of silicon nitride formation from $SiF_4/NH_3/H_2$ mixtures is controlled by the SiF_4 partial pressure.

Finally, the application of an r.f. plasma in a remote configuration improves the deposition process, the rate depending on the distance from the induction coil to the substrate. The higher the power density, the higher is the deposition rate, as a consequence of the increase in the electron temperature inside the plasma.

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