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REMOTE Plasma Chemical VaPouR DEPOSITION OF SiLICOn NiTRiDE FiLMs

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Abstract. - The relatively new technique of remote plasma enhanced chemical vapour deposition (RPECVD) of silicon nitride films is described. The influence of varying deposition parameters such as the ratios of reactant gases, pressure, temperature, and RF-power on the growth rate is described. Refractive index and amount of bonded hydrogen in the deposited films determined by IR attenuated total reflectance method are studied. The total concentration of bonded hydrogen in the deposited films was in the range 2 - 5 \times 10^{22} \text{ cm}^{-3}. The damage to a gateless GaAs FET after remote plasma deposition of silicon nitride films is negligible.

1. - Introduction.

The growing interest in plasma processing has motivated recent extensive studies on plasma chemistry [1], and numerous types of plasma deposition systems are now being used in the electronic industry [2]. The conventional approach to PECVD is based on the use of parallel plate reactors which use a capacitive coupling of RF power into a glow discharge. Such processes are widely employed to produce dielectric films at low temperature. In these techniques, however, defects are likely to be generated near the semiconductor surface due to plasma ion bombardment, and complex reactions are induced due to the simultaneous production of many sorts of reacting species. Moreover, process parameters such as total pressure, gas flow, gas composition, dissipated RF power, RF frequency and substrate heating are all interrelated and difficult to individually control. The method of remote plasma chemical vapour deposition is of great interest because it is an approach that circumvents some of these problems. In this relatively new technique only one of the reacting species (usually that which is not readily thermally decomposed) is RF [3, 4] or ECR [5]
excited and then mixed with the other reactants. The substrate is placed out with the region of which temperature is not the sole source of energy that is necessary to promote surface reactions. The deposition process is intend enhanced by the controlled formation in a plasma of active gas-phase species which are directed to the substrate. In this case the interrelation of process parameters is less and the probability of ion bombardment of the semiconductor surface and the growing film is substantially decreased.

We have investigated the remote plasma chemical vapour deposition of silicon nitride films since there is much interest in thin film dielectrics that can be deposited at relatively low temperatures (150 - 350 °C) for semiconductor applications. Although early paper on RPECVD dealt with silicon nitride films [3, 4] information on the characteristics and composition of the layers is not yet sufficient to evaluate the possibility of using these films for device applications. The main purpose of the present work is to establish correlations between the deposition conditions and the growth rate and characteristics of the films.

Fig. 1. - Schematic representation of the reaction chamber.
2. - Experimental details.

The silicon nitride films were deposited in a specially constructed deposition system. Figure 1 illustrates the construction of the reaction chamber. The RF power is coupled into the system inductively at a frequency of 1.76 MHz using an RF generator with a maximum output power of about 2 kW. A 4% SiH₄+Ar mixture and N₂/Ar (high purity) were used as source gases. The excited species (of nitrogen and argon) are brought into the top of the chamber after inductive excitation. The diameter of the excitation tube is 6 cm and that of the deposition chamber is 18 cm. Typical gas flow rates were 50-150 SCCM for nitrogen feed line. The silane-argon mixture was brought directly into the main reactor where it mixed with the excited species. Gas flow rates of the silane-argon mixture were 0.5-50 SCCM. The silicon nitride films were deposited onto a substrate heated to 150-350 °C at an operating pressure in the range 35-130 Pa. The distance between the dispersal ring (through which the silane-argon mixture was introduced) and the substrate surface was about 8 cm. The chamber was evacuated to a pressure of 10⁻³ Pa and heated to 200 °C for desorption of residual gases from the chamber walls prior to all depositions.

3. - Experimental results and discussion.

To achieve a better understanding of the chemistry of layer formation and the effect of process parameters on film properties we have investigated the composition of plasmas in the chamber near the substrate using emission spectroscopy of the chemiluminescence observed during the RPECVD of the silicon nitride films. These spectra showed that, beside excited molecules and ions of Ar and H₂, N₂⁺ molecules (in excited C²Πu and B³Πg states), N₂⁺ and N⁺ ions and very probably SiH radicals are present in the reaction zone. It was at a fixed power found that the growth rate of the films is roughly proportional to the emission intensity of the so-called first and second positive systems of nitrogen. The pressure dependence of the optical emission intensity
of $N_2^*$ molecules and the silicon nitride deposition rate $V_{depl}$ are shown in Fig. 2.

![Fig. 2. Optical emission intensity of $N_2^*$ molecules and SiH radicals and nitride growth rate vs. total pressure.](image)

![Fig. 3. Optical emission intensity of $N_2^*$ molecules and deposition rate vs. RF-power.](image)

Figure 3 shows that power dependence of the deposition rate is not similar to that of deposition rate when RF power was low. We think that in this case all molecules of SiH$_4$ were excited and excess of RF power was coupled into the system. It was not possible to study the correlation between the growth rate and the intensity of the optical radiation corresponding to SiH radicals (414.2 nm) because this is a very weak signal. We have found the correlation between these factors only when we studied the pressure dependence (over the low pressures, see Fig. 2).

On the basis of the emission spectroscopy results an initial model of the silicon nitride formation can be made. We suggest that RPECVD involves two simultaneously occurring processes: a homogeneous process in the reaction zone (where silane and excited nitrogen are mixed) and a heterogeneous process at the substrate surface. The SiH radicals (the most important products of the first process) are formed
due to interactions of excited nitrogen molecules with nonactive SiH₄ molecules. The film formation is the result of a heterogeneous process and depends on production of excited nitrogen molecules and SiH radicals.

As is common for plasma activated processes the temperature of the substrate has no significant influence on deposition rate but the properties of the deposited films depend strongly on this parameter (see Fig. 4 and Fig. 5).

It is well known that the refractive index of silicon nitride films prepared by PECVD depends on the film composition [6]. The film with the stoichiometric composition has a refractive index of about 2.05-2.1 [6]. The refractive index decreases with increasing oxygen or bonded hydrogen [7]. We found that the values of refractive index for films deposited at low temperature are about 1.6-1.8. In order to find the reason for the change in properties of deposited films with temperature and other process parameters we have studied their composition using IR spectroscopy. A typical IR transmission spectrum of an RPECVD silicon nitride film is shown in Fig. 6(a).

![Fig. 4. Influence of substrate temperature on the refractive indices and breakdown fields of the deposited films.](image1)

![Fig. 5. Effect of substrate temperature on deposition rate and content of bonded hydrogen.](image2)
Fig. 6. - IR spectra of silicon nitride films deposited at 300 C. 1 - N$_2$SiH$_4$ ratio - 2500; 2 N$_2$/SiH$_4$ ratio - 1300; a - transmission spectra; b - spectra recorded by IR attenuated total reflectance method.

The spectrum shows at least three absorption peaks. The first at 3300-3350 cm$^{-1}$ is characteristic of N-H$_x$ (x = 1-2) bond stretching; the second at 2100-2250 cm$^{-1}$ is due to Si-H$_x$ (x = 1-2) bond stretching; and the third at about 845-870 cm$^{-1}$ is characteristic of Si-N bond stretching in silicon nitride. Absorption in the region of 1080 cm$^{-1}$ due to Si-O bond stretching is negligible. The results of SIMS analysis show that the concentration of oxygen and other impurities, excluding hydrogen, is insignificant. Thus it could be concluded that the chemically bonded hydrogen content certainly affects refractive index, breakdown fields and other properties.

We have also carried out a quantitative bonded hydrogen analysis of the SiN$_x$H$_y$ RPECVD films using the IR attenuated total reflectance method.
One of these spectra is shown in Fig. 6(b). The values of the calibration factors for calculation of hydrogen content have been taken from Lanford and Rand [8]. The total concentration of Si-H$_x$ and N-H$_x$ bonds is given in Fig. 5 as a function of temperature for the films deposited at a chamber pressure of 80 Pa and a N$_2$/SiH$_4$ ratio of 1200. Thus these results show that content of bonded hydrogen in the films probably affects all physical and chemical film properties.

The concentrations of Si-H$_x$ and N-H$_x$ bonds depend on the gas phase composition. In Fig. 6 the IR spectra of SiN$_x$H$_y$ RPECVD films deposited both at a low N$_2$/SiH$_4$ ratio of 1300 and a high N$_2$/SiH$_4$ ratio of 2500 are shown. It can be noted that the areas of the Si-H$_x$ and N-H$_x$ peaks in these spectra are different. Figure 7 shows the variation of the Si-H$_x$ and N-H$_x$ contents with the N$_2$/SiH$_4$ ratio. The total concentration of bonded hydrogen in RPECVD films deposited at 300 C was in the range 2-5 $10^{22}$ cm$^{-3}$. The refractive index increases from 2.1 to 2.9 with decrease of the N$_2$/SiH$_4$ ratio from 1400 to 300. Thus one can suggest that the concentration of Si-H$_x$ bonds increases as film becomes more silicon rich. When the N$_2$/SiH$_4$ ratio increases from 1800 to 2500 the refractive index decreases from 2.05 to 1.6 and in this case the film, probably, becomes nitrogen rich.

The films with lowest bonded hydrogen content and good dielectric and chemical properties were deposited at a N$_2$/SiH$_4$ ratio of about 1400-1800, at an operating pressure of 40-60 Pa and at temperatures in the region of 250-350 C. It should be noted that there is a striking contrast between the values of bonded hydrogen content in the RPECVD silicon nitride films in the present work and these described by Lucovscy et al. [3].

They assert that "hydrogen-free" films have been deposited by the RPECVD technique. We think the employing of usual transmission IR spectroscopy for thin (thickness about 100-130 nm) films does not realistically evaluate hydrogen content.

In order to evaluate the possibility of device applications for RPECVD silicon nitride films we have used them as a GaAs annealing encapsulant. We found that the films with high content of hydrogen decomposed during annealing. In this case the thickness of the films decreases during annealing and signs of failure arise. During annealing the concentration of hydrogen in the films reduced from 5 $10^{22}$ cm$^{-3}$. to
Fig. 7 - Effect of \( \frac{N_2}{SiH_4} \) ratio on deposition rate and content of bonded hydrogen.

about 0.4 \( 10^{22} \) cm\(^{-3} \) The films with the lowest bonded hydrogen content of 2 \( 10^{22} \) cm\(^{-3} \) were the most thermally stable. In this case films change in thickness by approximately 15-20 %. Results show the best thickness for a cap is 70-90 nm. It is interesting to note that the Si-H\(_2\) bonds are the most thermally stable and N-H\(_2\) bonds are more thermally stable than N-H bonds during annealing. It is in agreement with results of Maeda et al. [9]. For the purpose of defining the influence of exposure to plasma process on the semiconductor substrate surface we prepared silicon nitride films on standard gateless GaAs structures with a etched N\(^+\) contact layer using both conventional PECVD and RPECVD processes. When conventional PECVD is used the gateless saturation current after deposition decreases by 30-45 %. No decrease of saturation current was observed after the remote plasma chemical vapour deposition of silicon nitride films.
3. - Conclusions.

The refractive index and the concentrations of N-N$_2$ and Si-H$_x$ bonds were measured for silicon nitride films formed by the remote plasma CVD process from SiH$_4$ - N$_2$ - Ar gas mixture under different deposition conditions. The film composition and the content of bonded hydrogen depended strongly on the deposition conditions. The excellent dielectric properties were shown to correspond to the conditions for attaining films with the composition near stoichiometry as well as the lowest amount of the incorporated hydrogen. The lowest content of bonded hydrogen in the silicon nitride films was about 2 $10^{22}$ cm$^{-3}$. It has been shown that silicon nitride films deposited by remote plasma CVD have considerable potential for semiconductor applications.

References