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Deposition of low temperature Si-based insulators by the electron cyclotron resonance plasma method

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Abstract

The influence of the gas flow ratio (R) (O_2/SiH_4 and N_2/SiH_4) and the deposition temperature on the physical properties of SiO_y and SiN_x:H thin films deposited by the ECR–CVD method is analyzed. Two deposition regimes limited by $R = 1$, are found for SiO_y films. At $R < 1$, films are very Si-rich in nature, with [O]/[Si] ratios as low as 0.55. At $R > 1$, the [O]/[Si] ratio varies between 1.69 and 1.88 and the full width at half maximum of the Si–O stretching peak is almost kept constant at 90 cm^{-1}. The effect of increasing substrate temperatures is mainly to promote a nearest stoichiometric character of the films. The two deposition regimes described agree with the optical diagnosis of the discharge, that present Si related species in those created at $R < 1$, and OH and O_2^+ species in those created at $R > 1$. A similar trend is observed for the deposition of SiN_x:H films, for which the limiting gas flow ratio is also $R = 1$. At $R < 1$, the films are very Si-rich ($x \leq 0.38$), meanwhile at $R > 1$, the composition corresponds to near stoichiometric and N-rich films ($x = 0.91$–1.49). The main effect of the substrate temperature is to reduce the hydrogen content of the films. Both SiO_y and SiN_x:H films are used in Si-based MIS structures, for those the minimum density of interface states is 3×10^{11} cm^{-2} eV^{-1}. © 1998 Elsevier Science S.A.

Keywords: Deposition process; Electron cyclotron resonance plasma

1. Introduction

Thin films of SiO_y and SiN_x:H deposited at low substrate temperatures (≤ 200°C) have demonstrated their potential applications in device structures based on silicon and on III–V compound semiconductors [1]. In recent years, one of the most useful plasma methods used to obtain these films has been the electron cyclotron resonance plasma deposition method (ECR–CVD) [2,3]. The results published at this time using this method are mainly focused on near stoichiometric films. In this paper, we compare the deposition of SiO_y and SiN_x:H films using the ECR–CVD method and a wide variety of deposition conditions which results in films with different stoichiometries.

2. Experimental

The deposition system consists of a commercial reactor divergent type, attached to a deposition chamber of our design. The gases used for the SiO_y deposition were O_2 and SiH_4. For the SiN_x:H deposition, the O_2 gas was substituted with N_2. The gas flow ratios O_2/SiH_4 and N_2/SiH_4 (R) changed between 0.5 and 20, and between 0.5 and 9, respectively. The deposition temperature was varied between 50°C and 200°C. Microwave power and deposition pressure were kept constant at 100 W and 2 mTorr, respectively. Auger Electron Spectroscopy was used to measure the [O]/[Si] and [N]/[Si] ratios in the SiO_y and SiN_x:H films, respectively. Infrared absorption spectroscopy (FTIR) was used to study the bonding structure of both films and to measure the hydrogen content of the SiN_x:H films [4]. In order to characterize the discharge, optical diagnosis spectroscopy was used. The spectra are recorded through a quartz window by using a monochromator (Jovin Ivon H25) operating in the 200–800 nm wavelength range, and they correspond to the whole downstream plasma volume.

3. Deposition of SiO_y films

Fig. 1 shows two optical diagnosis spectra of the discharges created at different O_2/SiH_4 gas flow ratios,

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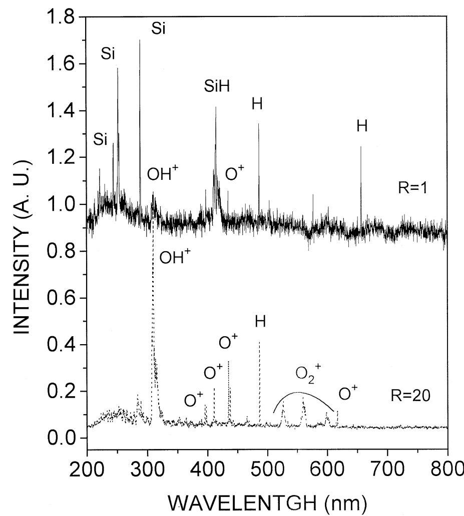

Fig. 1. Optical diagnosis spectra of the discharges created at O_2/SiH_4 gases flow ratio $R = 1$ and $R = 20$. The spectrum that corresponds to $R = 1$ is shifted in the y axis for clarity.

$R = 1$ and $R = 20$. For those created at $R = 20$, the most intense peak corresponds to the molecular specie OH^+, and the rest of the peaks are mainly related to the oxygen gas used in the discharge, such as different atomic species O^+ and the triplet peak corresponding to the O_2^+ molecule. The high efficiency and high ionization ratio of the ECR plasma method is demonstrated in the spectra as the O_2 molecules appeared dissociated either as atomic oxygen O^+ or ionized as O_2^+ molecules. The OH^+ molecule observed also indicates a high efficiency for vapor phase reactions, and the most probable origin of this molecule are the reactions between atomic oxygen coming from the O_2 molecules and H evolved from the decomposition of the SiH_4 molecules in SiH_n radicals ($n = 0$–3) and H atoms. It is difficult to relate this molecule to other sources, such as the presence of H_2O in the deposition chamber due to a poor base pressure, as it has not been observed in N_2/SiH_4 discharges formed at similar conditions. Different species are observed in the spectra of the discharge created at $R = 1$, since the peaks are mainly related to Si. In this case, the OH^+ molecule is hardly observed in the spectra, while the most intense peak corresponds to atomic Si according to the high SiH_4 flow of the discharges generated at low R values. Peaks corresponding to the SiH molecule and atomic H are also observed, which confirms the decomposition of the SiH_4 molecules in SiH_n radicals and H atoms.

Fig. 2a presents the [O]/[Si] ratio of the SiO_y films as a function of the gas flow ratio for those films deposited at 50°C, and includes some results obtained at 200°C. Two different deposition regimes (separated by $R = 1$) can be concluded for films deposited at 50°C. Those films deposited at $R < 1$ are silicon-rich, with [O]/[Si] ratios as low as 0.55. At $R = 1$, the [O]/[Si] ratio suddenly increases, obtaining a plateau of about 1.8 in this ratio for higher R values. Fig. 2b presents the full width at half maximum (FWHM) of the Si–O stretching vibration mode as a function of the gas flow ratio for films deposited at three different temperatures. For those deposited at 50°C, the two different deposition regimes are also observed in this figure. The high FWHM value of films deposited at $R < 1$ is explained as a dispersion of the bonding angles of the system Si–O–Si, caused by induction effects of the Si neighbors on the system [5]. For $R > 1$, the FWHM is nearly constant at a value (~ 90 cm^{-1}) close to that corresponding to thermal SiO_2 films.

The two deposition regimes deduced from the film characteristics are well related to the radical species observed in the optical diagnosis of the discharge. At $R \leq 1$, the plasma species are mainly related to silicon, and the absence of oxygen related species, caused by the low oxygen flow, results in silicon-rich films. At $R > 1$, the oxygen flow is high enough to promote oxygen incorporation into the film, in agreement with the presence of oxygen-related species in the optical diagnosis spectra. The films deposited at 50°C and $R > 1$ have similar properties to those reported in the literature for ECR–CVD SiO_y films deposited at different temperatures (≤ 200°C) [6,7]. However, there is no evidence in the literature of the two different deposition regimes observed in this study, probably because the different authors mainly focus on deposition conditions resulting in near stoichiometric films.

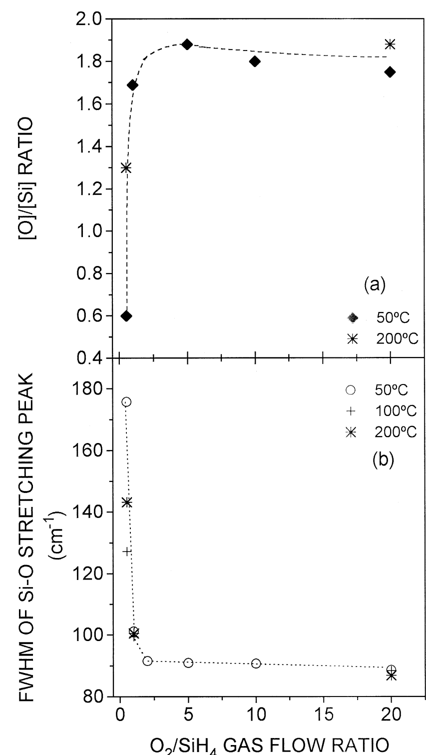

Fig. 2. (a) [O]/[Si] ratio of the SiO_y films deposited at 50°C (◆) and 200°C (*) as a function of the gases flow ratio R. (b) FWHM of the Si–O stretching peak for the SiO_y films deposited at 50°C (○), 100°C (+) and 200°C (*) as a function of the O_2/SiH_4 gases flow ratio.

The effect of increasing deposition temperatures on the film characteristics can be observed in Fig. 2a,b, which include the data of films deposited at different temperatures. At $R > 1$, the increase of the temperature up to 200°C has a small influence on the film characteristics. The FWHM of the Si–O stretching peak is not affected by this parameter, and the [O]/[Si] ratio slightly increases when the temperature changes from 50°C to 200°C. At $R < 1$, the increase of temperature seems to activate the thermal reactions on the substrate, and to contribute with an additional energy to the reaction between species, as indicated by the increase of the [O]/[Si] ratio and the clear decrease of the FWHM of the Si–O stretching peak. Deposition temperatures higher than 200°C are not investigated in this work, since the main objective is to use the SiO_y and SiN_x:H films in MIS structures based on InP.

4. Deposition of SiN_x:H films

Fig. 3 presents the [N]/[Si] ratio for SiN_x:H films deposited at different gas flow ratio N_2/SiH_4 and 200°C. Previous studies not included in this work indicate that the deposition temperature has no influence on the [N]/[Si] ratio of the films. The two deposition regimes observed for the SiO_y films deposited at 50°C are also observed for the SiN_x:H films deposited at 200°C. At this deposition temperature, the films obtained at $R < 1$ are very silicon-rich films, while those obtained at higher R values can be considered as near stoichiometric films ($x = 0.91–1.41$) and nitrogen-rich films ($x = 1.46–1.49$) [8,9]. Differences between the deposition characteristics of SiO_y and SiN_x:H films are found at high R values. In fact, N_2/SiH_4 ratios higher than 5 result in nitrogen-rich films, which indicates a high activation of the N_2 gas in the discharge. On the contrary, as it has been described in previous paragraphs, the deposition of SiO_y films at similar O_2/SiH_4 ratios results in [O]/[Si] values lower than $y = 2$.

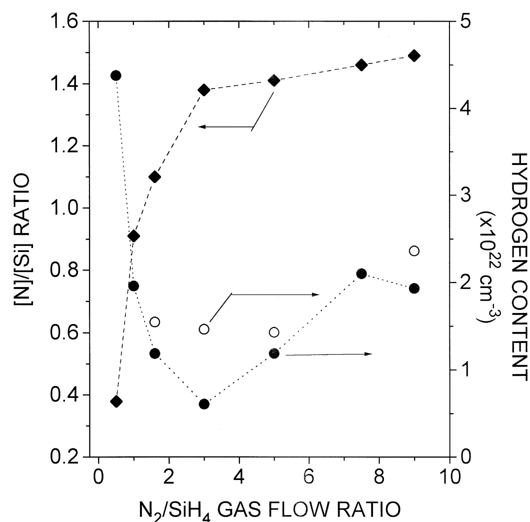

Fig. 3. [N]/[Si] ratio (◆) and hydrogen content for SiN_x:H films deposited at 50°C (○) and 200°C (●) as a function of the N_2/SiH_4 ratio. The [N]/[Si] ratio corresponds to films deposited at 200°C.

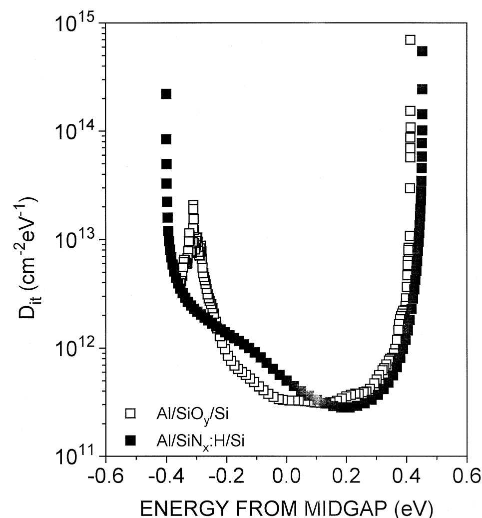

Fig. 4. Distribution of the density of interfacial states in the silicon gap energy for MIS structures fabricated on Si using as insulator SiO_y films (□) and SiN_x:H films (■) deposited at 200°C and $R = 20$ and $R = 3$, respectively. The gap energy is measured from the midgap.

Fig. 3 includes the hydrogen content measured in the SiN_x:H films deposited at 50°C and 200°C as a function of R. For all films considered, the hydrogen content decreases when the deposition temperature increases as is expected from previous results in the literature for SiN_x:H plasma deposited films [10]. For both temperatures, the hydrogen content has a minimum value at $R = 3–5$ which corresponds to near stoichiometric films ($x = 1.38–1.41$). The lowest Si–H and N–H bond densities are found at $R = 3–5$, which explains the minimum hydrogen content at this gas flow ratio [11,12].

5. MIS structures

Both SiO_y and SiN_x:H films have been used as insulators in silicon based MIS structures. Fig. 4 presents the density of interfacial states distribution as a function of the gap energy measured for MIS structures fabricated using both SiO_y and SiN_x:H films. Both films are deposited at 200°C and at $R = 20$ and $R = 3$, respectively, which corresponds to the [O]/[Si] and [N]/[Si] ratios nearest to the stoichiometric value of all films considered. For $Al/SiO_y/Si$ structures, the minimum D_{it} value ($\sim 3.00 \times 10^{11}$ cm^2 eV^{-1}) is higher than those reported in the literature for plasma deposited SiO_y films [13]. For Al/SiN_x:H/Si structures, the D_{it} values are between the better ones reported in the literature [14], which shows the

suitability of the SiN_x:H films deposited by the ECR–CVD method to be used in silicon based device structures. Moreover, the D_{it} distribution for the Al/SiN_x:H/Si structures is extended in almost the whole energy gap, which demonstrates the absence of traps that pinch off the Fermi level, and the quality of the interface SiN_x:H/Si obtained by the ECR–CVD method. The results of the application of SiN_x:H films in InP based MIS structures will be presented in future works.

6. Conclusions

Two deposition regimes have been observed for SiO_y and SiN_x:H films deposited by the ECR–CVD method, limited by the gas flow ratio $R=1$. Films deposited at $R<1$ are very silicon-rich, whereas the [O]/[Si] and [N]/[Si] ratio abruptly increase at higher R values. Differences between the deposition mechanism of both type of films are observed at $R \geq 5$. At these gas flow ratios, the SiN_x:H films obtained are nitrogen-rich, while the [O]/[Si] ratio of the SiO_y films is lower than 2, which demonstrates a low activation of the O_2 gas. The effect of increasing deposition temperatures is to increase the [O]/[Si] ratio of the SiO_y films, and to reduce the hydrogen content of the SiN_x:H films. The application of both type of films in devices structures is demonstrated by the low density of interfacial states measured in silicon based MIS structures.

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