Electrical Properties of MIM and MIS Structure using Carbon Nitride Films

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(Received June 26 2006, Accepted August 16 2006)

Nano-structured carbon nitride (CN_x) films were prepared by reactive RF magnetron sputtering with a DC bias at various deposition conditions, and the physical and electrical properties were investigated. FTIR spectrum indicated an α-C_3N_4 peak in the films. The carbon nitride film deposited on Si substrate had a nano-structured surface morphology. The grain size was about 20 nm and the deposition rate was 1.7 μm/hr. When the N_2/Ar ratio was 3/7, the level of nitrogen incorporation was 34.3 at%. The film had a low dielectric constant. The metal-insulator-semiconductor (MIS) capacitors that the carbon nitride was deposited as insulators, exhibited a typical C-V characteristics.

Keywords : Nano-structure, Carbon nitride, RF magnetron sputter, MIS capacitors

1. INTRODUCTION

Research on carbon nitride has focusing mainly on synthesizing the superhard β-C_3N_4 phase that was theoretically predicted by Liu and Cohen[1]. Carbon nitride was compared with the well-understood compound silicon nitride, with the expectation of the potentially useful mechanical and electrical properties such as a high hardness and semiconductivity. The calculated bond length (1.47 Å) and low ionic character (~7 %) suggested that its bulk modulus and hardness would be close to those of diamond. The predicted cohesive energy of 5.8 eV per atom suggests that there is a good chance that β-C_3N_4 is at least a metastable structure. The good agreement between the structural properties of β-Si_3N_4 calculated using the same method and the experimental values supports these predictions[2].

In ultra large-scale integrated circuits (ULSI), the dielectric constant of the insulation membrane is an important parameter that is related to the interconnection delay. Amorphous carbon nitride films, a-CN_x, are candidates for interlayer insulator materials in ULSI. The most important property of insulators for ULSI application is a low dielectric constant[3-5].

In this study, the electrical properties of carbon nitride films produced by reactive sputtering were examined as a function of the deposition conditions and the bonding structure of the films. This paper reports the electrical properties of Al/CN_x/Al and Al/CN_x/p-Si structures through the dielectric and capacitance-voltage (C-V) characteristics.

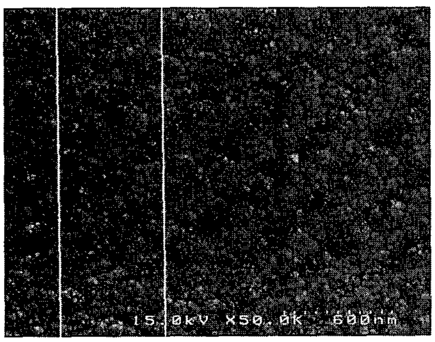
2. EXPERMENTAL

The films were deposited by reactive RF magnetron sputtering. The use of a Nd-Fe-B magnet ensures a very high flux density in between the substrate and target region[6]. A high-purity 99.997 % graphite planar target was mounted at a distance of 6 cm from the substrate and different N_2/Ar gas mixtures were used as the sputtering gases to vary the film compositions. The gas purity was 99.999 % in each case. Prior to deposition, the substrates were cleaned with acetone and methanol in an ultrasonic bath. All the substrates were cleaned by an RF glow discharge of Ar for 5 min to remove any residual contaminants. Flow rate ratio of N_2/Ar for film formation was varied with 0/10, 3/7, 5/5, 7/3, and 10/0. Other deposition conditions of the carbon nitride films were fixed as follows; RF power: 200 W, substrate bias: -60 V (DC), temperature: 200 ℃, deposition time: 60 min, working pressure: 5 mTorr[7]. Before the fabricating the MIS capacitors, the resistivity of the deposited films was obtained from the I-V characteristics using the metal-insulator-metal (MIM) structure on the quartz substrate. Aluminum electrodes were prepared by vacuum evaporation before and after deposition of the CN_x films. The electrical measurements were performed at room temperature using CATS CA-EDA semiconductor analyzer and FLUKE PM6306 RCL Meter.

For an ohmic contact of MIS devices, the lower electrode was formed on the p-type Si (100) backside by an aluminum alloy after etching of native oxide. The upper metal contacts were fabricated by evaporation of 6 mm diameter Al dots in a high vacuum system with masks. The capacitance was measured with an HP-4280A C-V plotter. All the characterizations of the deposited films were performed ex situ. The atomic ratio of N to C, N/C, was determined by XPS (VG XR705) with Mg K_α X-ray radiation. The surface and bond structure of the film were analyzed with scanning electron microscope (SEM, HITACHI S-4200) and FTIR (Research I series Mattson).

3. RESULTS AND DISCUSSION

Figure 1 shows the surface (a) and cross-sectional (b) SEM images of the deposited film that was formed in the reactive RF magnetron sputtering for 1 hr. The carbon nitride film deposited on the Si substrate has a uniform nano-structured surface morphology (Fig. 1(a)). The average grain size is about 20 nm and the deposition rate is about 1.7 μm/hr. The formation of SiC and/or SiCN interlayer is observed, which is promoted by the reactions between the plasma carbon and nitrogen gaseous species with the silicon atoms from substrate [8].



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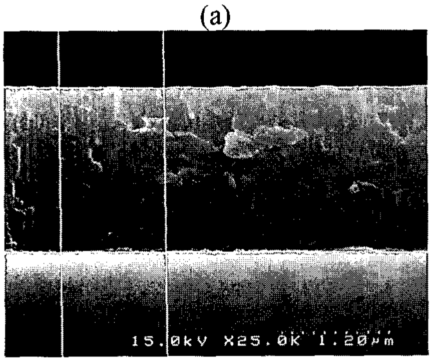

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Fig. 1. Surface (a) and cross-sectional morphology (b) of carbon nitride film deposited on Si substrate.

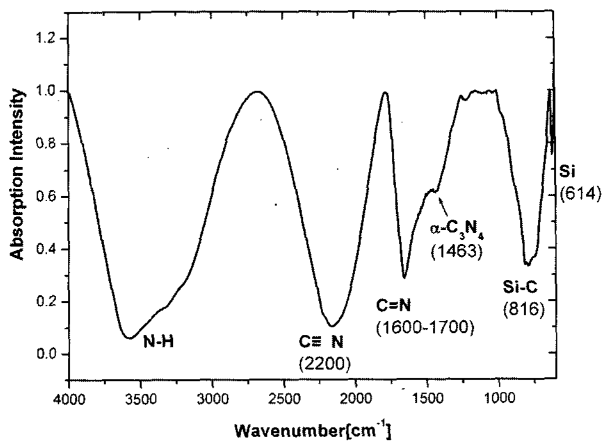


Fig. 2. FTIR spectrum of the carbon nitride film.

Figure 2 shows the FTIR spectrum of a carbon nitride film deposited on the Si substrate. Kaufman *et al.*[9] reported that nitrogen substitution is responsible for breaking the symmetry of the E_{2g} mode and the intensity of the G and D bands. The band at ~2200 cm^{-1} is assigned to approximately stretching vibration of the C≡N bond. The C=N stretching band (sp^2 line) appears at between 1600~1700 cm^{-1} depending on the level of nitrogen incorporation in the film[10,11]. The C≡N, C=N and α-C_3N_4 peaks[12] can be seen at 2200 cm^{-1}, 1656 cm^{-1} and 1483 cm^{-1}, respectively. The broad peak (3000 cm^{-1}- 4000 cm^{-1}) is due to the N-H stretching band (wave number of 3300 cm^{-1})[13]. This band is the result of residual water vapor in sputtering chamber during the film deposition. Hydrogen bond is commonly observed in porous materials and it is probably a good indicator of the softness of films. A Si-C peak at 816 cm^{-1} is due to the interlayer with carbon and the Si substrate, as shown in Fig. 1. This means that excess nitrogen is present as an IR invisible bond, such as a non-polar bond.

X-ray photoelectron spectroscopy (XPS) is based on measuring the binding energy of the core-level electrons ejected from the sample surface, as a consequence of monochromatic X-ray irradiation. Figure 3 shows N(1s) and C(1s) X-ray photoelectron spectra of the carbon nitride film. The spectrum can be deconvoluted into three or four peaks as is normally found. The N(1s) peaks have been assigned as C≡N (sp) at ~398.8 eV, C=N (sp^2) at ~ 400 eV and N-N (sp^2) at ~401 eV for the film containing ~32.7 at.% N as shown in Fig. 3(a). The peak at ~401.2 eV, which is typically assigned to N-N or N-O bonding, is found to increase with the nitrogen content of the films. Since there is no observable oxygen in the films, the 401.2 eV peak can be assigned to N-N bonds. This behavior confirms the hypothesis of[2] that the excess nitrogen in the films is in some IR-inactive bonding structure, in fact, it is in the form of N-N bonds.

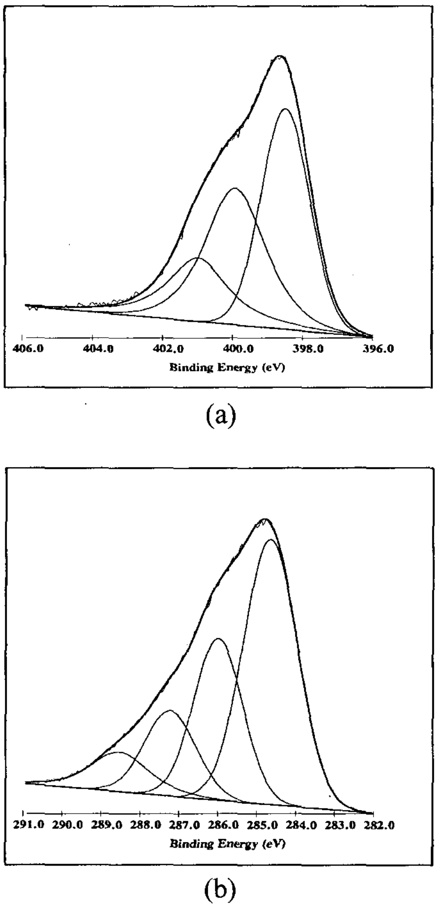


Fig. 3. X-ray photoelectron spectrum of CN_x film, (a) N(1s) electrons and (b) C(1s) electrons. The spectrum obtained is deconvoluted into peaks using Gaussian-Lorentzian fit.

Inferences may also be drawn from the behavior of the C(1s) peak in Fig. 3(b). Deconvolution shows the existence of four peaks at 285.8 eV (sp^2), 287.1 eV (sp^3), 288.5 eV (sp) and 284.5 eV. The peak at 284.5 has been generally labeled as due to adventitious carbon (AC) mainly due to atmospheric contamination[14]. Because of no evidence of sp^3 C-N bonding in the films, it is ascribed that the 287.1 eV peak purely due to C-C bonds, and the others will be due to a combination of carbon-carbon and carbon-nitrogen bonds.

The chemical composition of a carbon nitride films as a function of the N_2/Ar ratio is shown in Fig. 4. As the increase of the nitrogen gas concentration, the level of nitrogen incorporation in the film increases. This is probably due to the increased sputtering rate of the C species from the target, as the steady state N concentration on the target surface increases. Energetic or neutral Ar species enhance the mobility of the nitrogen species, and increase the level of N sticking at

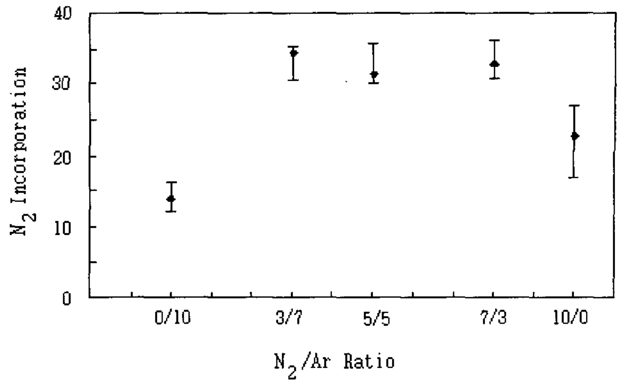


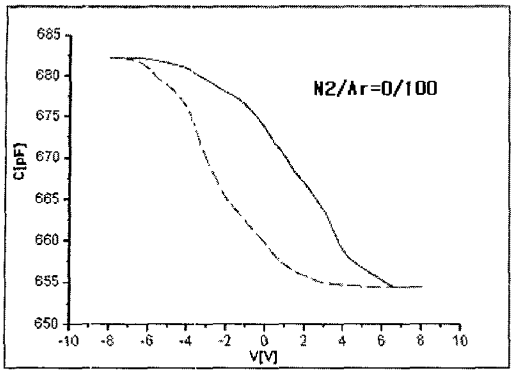
Fig. 4. Chemical composition of the carbon nitride film as a function of N_2/Ar ratio.

the film surface[15]. When the N_2/Ar ratio range is 3/7-7/3, a relatively high level of nitrogen incorporation is obtained, nevertheless, these film do not reach the stoichiometric composition of the calculated carbon nitride. If the nitrogen gas was used only as the sputtering media, the nitrogen incorporation of the film is lower than 7/3 N_2/Ar ratio. The addition of argon in the sputtering gas mixture should enhance the sputtering rate of graphite from the target, because the sputtering yield of graphite by Ar gas is expected to be higher due to higher mass. Both energetic and neutral Ar species probably enhance the nitrogen species' mobility and increase N sticking at the growth surface. Unwanted nitrogen incorporation appears in the 0/10 N_2/Ar ratio. We can consider that carbon nitride around the carbon target is sputtered during the subsequent sputtering process regardless of the pre-sputtering.

The dielectric constant of the deposited carbon nitride films with MIM (metal-insulator-metal) structure is measured by an RCL meter at 1 MHz. Table 1 shows the dielectric constant of the carbon nitride films at different N_2/Ar ratios. The CN_x films had a low dielectric constant in the range of 1.64 to 3.73. The dielectric constant depends on the N_2/Ar ratio. Low-*k* materials are needed for the back end of the line (BEOL) interconnect structures of the ULSI in order to improve their performance. Diamond, which is a prominent candidate, has a dielectric constant of 5.6, which is higher than that

Table 1. Dielectric constant of the carbon nitride films as a function of the N_2/Ar ratio.

N_2/Ar ratio	0/10	3/7	5/5	7/3	10/0
Dielectric constant	1.64	3.21	3.69	3.73	6.06



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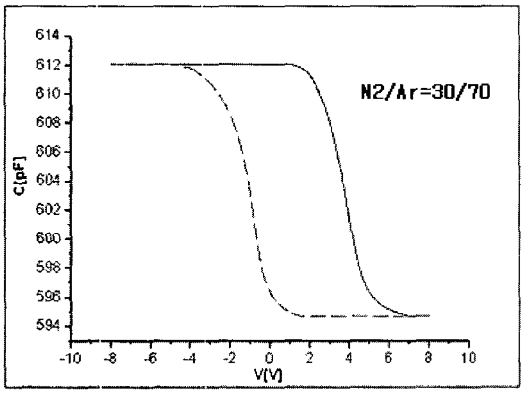

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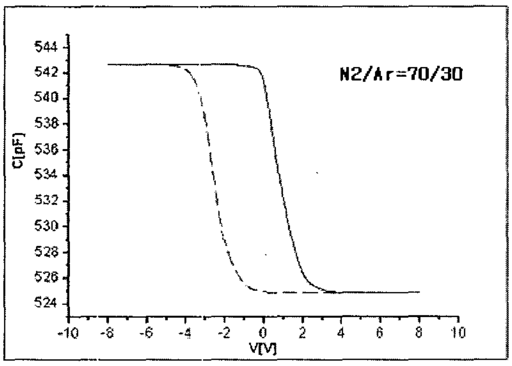

(c)

Fig. 5. C-V plot of MIS capacitors using carbon nitride films as a function of the N_2/Ar ratio; (a) 0/100, (b) 30/70 and (c) 70/30.

of SiO_2 (k=4)[16]. We may expect that carbon nitride films, which have a low dielectric constant, can be used as insulating materials for the ULSI interconnects.

Figure 5 shows the capacitance-voltage characteristics of the carbon nitride MIS capacitors with the N_2/Ar ratio. Over the bias range from -6 to 8 V under a modulation frequency of 1 MHz, we obtained a C-V curve which shows three distinct steps as well as conventional MIS capacitors. The minimum capacitance of the $Al/CN_x/Si$ structure is expressed as follows:

$$C_{min} = C_{CN}C_s/(C_{CN}+C_s) = C_{CN}/(1+(k_{CN}W/k_s d)) \quad (1)$$

where, C_{CN} and C_S are the capacitance per unit area of the CN_x film and Si substrate, k_{CN} and k_s are the permittivity of the CN_x and Si, d is thickness of the CN_x film and W is depletion layer width of Si, respectively. Using full-depletion approximation, we know the capacitance of carbon nitride MIS capacitor is inversely proportional to the total depletion layer width W from equation (1). A direct consequence is that the threshold voltage should decrease when increasing the N_2/Ar ratio in the growth conditions. This effect is mainly due to the reduction of the energy band gap with nitrogen incorporation. The bulk potential $\Phi_F=E_{Fi}-E_F$, which is directly related to the threshold voltage, is found to decrease with N_2/Ar ratio. The flat band voltage and threshold voltage in the 70/30 N_2/Ar ratio are about 0.5 and 2.9 V, respectively, in Fig. 5(c). We can find the voltage shift in C-V response. Initially, the flat band voltage is high, and after positive bias aging it shifts to negative. With negative bias aging, the flat band voltage returns to its original value. These results are mainly attributed to mobile ion movement that alters the centroid of the mobile ion distribution[17]. Initially, the ions are concentrated at the metal-CN_x interface. Because most of the ionic charge is imaged in the gate rather than the silicon, the initial C-V curve has high flat band voltage. During positive gate bias aging, ions drift from the metal-CN_x interface to silicon-CN_x interface so that almost all the ionic charge is imaged in the silicon producing the shift shown by dotted curve in Fig. 5. Aging with negative gate bias, ions drift from the metal-CN_x interface to the silicon-CN_x condition. An inversion state is not found in Fig. 5(a), because this film is similar to the conducting carbon from the incomplete supply of nitrogen. Deep depletion is also observed due to interface trap charges and leakage current.

4. CONCLUSION

The nano-structured carbon nitride films by reactive RF magnetron sputtering system showed C≡N, C=N and α-C_3N_4 FTIR peaks at 2200 cm^{-1}, 1656 cm^{-1} and 1483 cm^{-1}. When the N_2/Ar ratio range is 3/7-7/3, a relatively high level of nitrogen incorporation is obtained, nevertheless, these film do not reach the stoichiometric composition of the calculated carbon nitride. Carbon nitride films with MIM structure had a low dielectric constant. The dielectric constant depended on the N_2/Ar ratio. The MIS capacitors, which used the carbon nitride as insulator, exhibited a typical C-V characteristics. The carbon nitride film, which has a low dielectric constant (approximately 3), can be used as an insulating material for ULSI interconnects.

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