Low-K Carbon Films Deposited in Low Frequency Discharge for Sub-Micron Devices

A.Kosarev, A.Torres and C.Zuniga

Institute National for Astrophysics, Optics and Electronics, Puebla, P.O.Box 51&216,
Mexico 72000, akosarev @inaoep.mx

ABSTRACT

Low *K* carbon films (a-C:H_x) deposited in low frequency discharge have been studied. The films were deposited from methane-hydrogen mixture at discharge frequency f=*110 kHz*, substrate temperature T_s=*350 °C*, with variation of gas flow and discharge conditions. Chemical structure of the films was characterized by FTIR. Resistivity ρ, dielectric constant K and breakdown field E_b were measured in the films. It was found that *ρ. K* and E_b correlated with C=C and C-H bonding concentrations. High $\rho=10^{14}$ *Ohm*cm*, $E_b=1.5*10^6$ *V/cm* and low *K=2.1* were obtained in the films with optimal concentration of both C=C and C-H bonding. Current-voltage characteristics in high, pre-breakdown, field and dependence of breakdown on electrode material gave an evidence for Schottky emission mechanism for carrier transport before breakdown. After isothermal annealing at *T=400 °C* resulted in an increase of C=C and a reduction of C-H bonding concentration. While resistivity reduced by about order of magnitude and K increased from *K=2.1 to 3.1*.

Keywords: low-K materials, carbon films, plasma deposition

1 INTRODUCTION

The advancement of microelectronics needs to develop more and more highly integrated circuits. It is known [1,2] that interconnect delay begins to dominate total device delay time and consequently, operation rate at device size less than 0.2 μm, therefore a transition to low dielectric constant materials (low-*K* materials) is so attractive. The conventional used dielectric materials such as SiO_2 (*K=3.9*) and SiN (*K= 7.5*)[3] cannot meet these requirements. SEMATECH roadmap [4] predicted in 1998 K values in the range of 2.0 to 2.5. Some of bulk materials have similar values, e.g. poly-tetrafluorethylene (PTFE) K=2[5], polyethylene *K=2.3* [5]. Recent progress in low-K materials is quite encouraging. The lowest values of *K=1.3-2.5* in inorganic materials have been achieved in nano-porous silica [6], in porous polymers and PTEF *K=1.9* [6]. However, not any low-K dielectric materials can be incorporated into integrated circuits. These materials should meet many other requirements, including such important parameters as resistivity, breakdown field and thermal stability at about 400-450 C. The total amount of the properties required for interconnect dielectrics is about 37 [7]. Unfortunately it is difficult to find all the important parameters of new materials, which make comparing these materials difficult. As far as we know a perfect low-K material that meets all the requirements has not been found yet. The studied low-K materials are deposited by various methods. Among them plasma enhanced chemical vapor deposition (PE CVD) is a very attractive technique, because of compatibility to silicon technology and possibility of tailoring materials, including deposition of non-stechiometric compositions. Capacitive discharge at *f=13.5 MHz* is conventionally used in plasma deposition. Ion bombardment of the growing film is an important factor affecting electronic properties of the film [8,9]. Ion bombardment during growth is a key factor for diamond like carbon (DLC) film deposition [10]. Discharge with lower frequency will have thicker sheaths [11] resulting in higher ion bombardment. Budagian et al. [12, 13] studied a-SiC: H and a-C: H films deposited in low frequency (LF) plasma at *f=55 kHz*, however dielectric properties of the films have not been characterized.

The goal of this work is to study a correlation between deposition conditions, microstructure and such electrical characteristics as resistivity, dielectric constant and breakdown field in carbon films deposited by low frequency plasma.

2 EXPERIMENTAL

The films were deposited by low frequency PE CVD, *f=110 kHz*, in a capacitive reactor, using methane+ hydrogen gas mixtures, at the power *W= 200-300 W*, the substrate temperature T_s *=350 °C*, the flow rate *Q= 50-1000 sccm.* We used a modified AMP-3300 system of "Applied Material". The deposition rate was about 0.5 A/s, this value is close to that for typical PE CVD growth (~ 1A/s).

The films were deposited on the substrates of Corning 1737 glass for optical and electrical measurements, and on silicon wafers to form MIS structures. Si wafers (n-type, *ρ≈10 Ohm*cm*) were used as semiconductor in MIS structures. To form ohmic contact P ions were implanted into backside of the wafer. Then they were activated at 900 °C for 20 minutes in N_2 environment. This process provided a good ohmic contact with *Rs≈15 Ohm/□*. Before carbon

film deposition silicon oxide was removed by etching in buffered HF.

I(V) characteristics and *K* were measured in the sandwich type samples fabricated on both glass and silicon wafers. Electrodes of Al and Ti were deposited by electron gun evaporation with "Balzers -370". IR spectra were measured with "Vector 22, Bruker" Fourier spectrophotometer. *I(V)* characteristics were measured with "Keithley 2400" system.Thickness of the films was measured by "Tencor Alfa-step-200". We measured K with "1658 RLC Digebridge-2" AC bridge at frequency $f= 1kHz$ and from *C(V)* characteristics measured by "Keythley CV Analyzer-590" at 100 KHz. Annealing was conducted at $T=400$ °C in *Ar* atmosphere.

3 RESULTS AND DISCUSSION

Our previous experiments on effect of deposition conditions on microstructure and electrical characteristics of LF PE CVD carbon films indicated that it was possible to control both C=C and C-H bonding concentrations, $C_{C=C}$, C_{C-H}, and ρ, K and E_b by variation of the deposition conditions. Moreover it has been found that both $C_{C=C}$ and C_{C-H} should be optimized to obtain low K, high ρ and E_b [17].

It should be noted that for diamond like carbon films ion bombardment during growth is a very important factor [10]. In our case we deposited films at low frequency plasma, which provides higher bombardment then conventionally used RF plasma. All of the samples were deposited at relatively high substrate temperature $T_s= 350$ °C in contrast to many papers, in which this temperature was usually significantly less. We used higher temperature because of the requirements of further temperature processing of the films at temperatures in the range of 400-450 °C.

IR spectra of the studied films contained the lines as follows: at k≈2930 cm^{-1} assigned to CH_2 stretching mode (dominating line); and at k≈1600 cm^{-1} assigned to C=C stretching mode (dominating line) [14]. The characteristics of the lines, in particular, areas under the lines, which are proportional to the concentrations of the chemical bonds and, consequently, for $C-H_x$ modes to the concentration of hydrogen, are changed with deposition conditions. The samples with the best dielectric characteristics did not demonstrate the extreme values of hydrogen bonding or of C=C bonding.

As reported in ref. [17] there is a correlation between C_{C-H}, $C_{C=C}$ and ρ, K and E_b. The best parameters have been obtained with the optimal concentration of both C_{C-H} and $C_{C=C}$. From comparison between IR data and electrical characteristics, it has been suggested that the latter correlated with some material unit as $=C=H_2$. As it is shown in Fig.1, when the concentration of such units is the optimal the dielectric properties of the films are the best (the lowest-K, the highest resistivity and breakdown field).

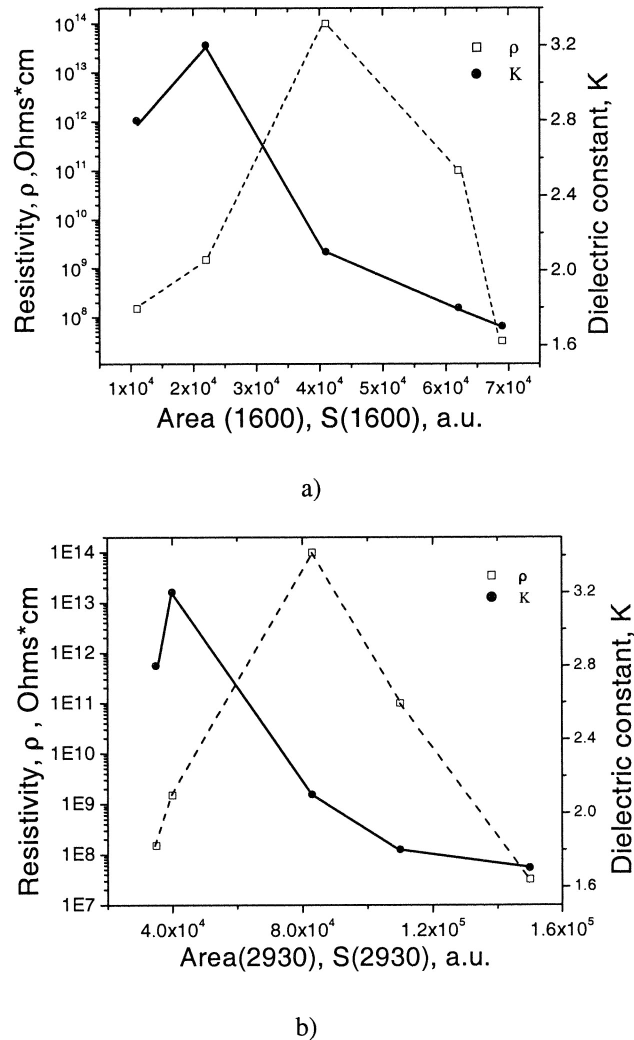


Figure 1. Resistivity ρ and dielectric constant K as a function of area of the line: a) at k=1600 cm^{-1} (C=C) and b) at k=2930 cm^{-1} ($C-H_x$).

In order to study the charge transport in the film we have measured current voltage *I(U)* characteristics at low and high electric fields up to breakdown and they are shown in Fig.2. At low field, in the range of voltage of $U = 0$ -40V, *I(U)* can be described as $I=kU^{\gamma}$, where γ is about 2-2.5, that indicates to space charge limited current of electrons [15]. At higher field *I(U)* characteristics significantly deviate from linear behavior in log-log scales. It means a change of the transport mechanism. In the insert in Fig.2 *I(U)* curve at high electric field is shown. It can be seen that in this region the current logarithm is proportional to square root of applied voltage. This behavior corresponds either to Schottky emission of electrons from an electrode or to Poole-Frenkel mechanism of carrier transport [3].

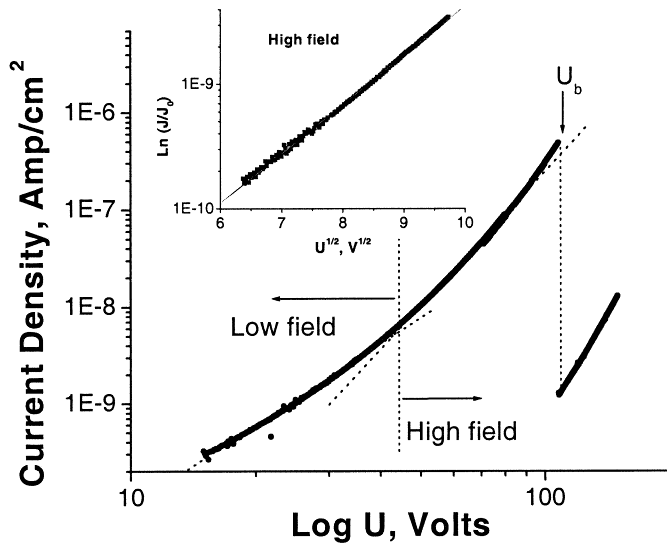


Figure 2. Current-voltage characteristics $J(U)$ in low and high field. In the insert high field $J(U)$ is replotted as $Ln(J/J_0)=f(\sqrt{U})$.

The current density in the Schottky emission can be written as

$$J=A^*T^2exp[(\beta_s\sqrt{U})/(kT\sqrt{d}) - e\Phi_S/kT] \qquad (1)$$

Where: $\beta_s = (e^3/4\pi\varepsilon_0 K)^{1/2}$, A^* is the Richardson constant, Φ_S is the contact barrier height, k is the Boltzman constant, e is the electron charge, ε_0 is the dielectric constant of free space, K is the film dielectric constant, T is the temperature, d is the dielectric film thickness.

In the case of Poole-Frenkel transport mechanism the current is due to field-enhanced excitation of electrons from the traps into the conduction band of the insulator. This current density is described by the equation

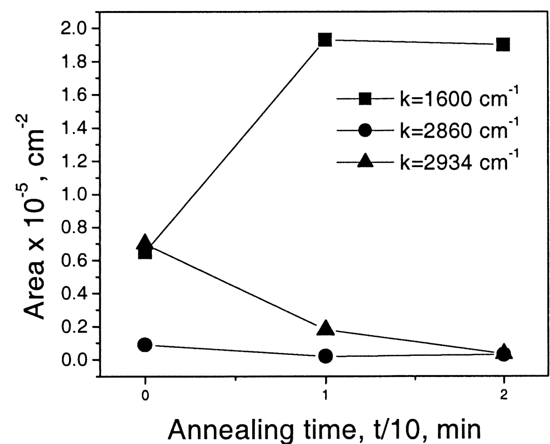
$$J=J_0exp[(\beta_{PF}\sqrt{U})/(kT\sqrt{d}) - e\Phi_{PF}/kT] \qquad (2)$$

Where $J_0=\sigma_0 E$ is the low field current density. It corresponds to $U\approx 40V$ in Fig.2 because from this point J(U) begins to deviate from the linear behavior in $LogJ=f(LogU)$ scale. σ_0 is the low field conductivity, $E=U/d$ is the applied electric field, $\beta_{PF} = (e^3/\pi\varepsilon_0 K)^{1/2}$, and Φ_{PF} is the height of trap potential barrier. It is evident that $\beta_{PF} = 2\beta_s$. This relationship allows us to distinct between the two mechanisms despite of virtual identity of the equations (1) and (2). The experimental points in the insert of Fig.2 can be best fitted by the following equation

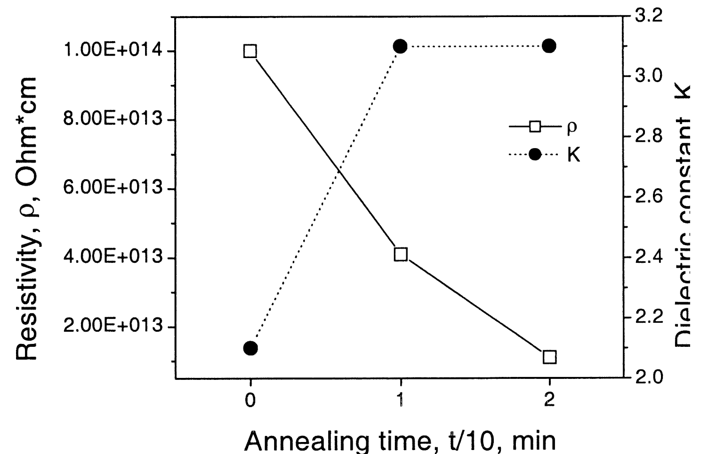
$$Ln (J/J_0) = A + B\sqrt{U} \qquad (3)$$

Where $A= -8$ and $B= 1.17\ V^{1/2}$. Now we can compare these experimental values with those calculated, inserting the thickness $d=0.7\mu m$ and $K=2.1$ for the sample #159.We shall obtain $B_s=\beta_s/(kT\sqrt{d}) \approx 1.19\ V^{1/2}$ and $B_{PF}\approx 2.38\ V^{1/2}$. Low indexes "s" and "PF" correspond to Schottky and Poole-Frenkel emissions, respectively. Experimental value of $B= 1.17\ V^{1/2}$ is close to B_s. This agreement and also our observation of top electrode metal effect on breakdown field give an evidence for Schottky emission transport mechanism in high pre-break-down field $E>2.5*10^5$ V/cm.. At some value of the electric field $E_b=U_b/d$ we observed a jump of the current by about of two orders of value. We identified this as the breakdown. Such behavior is known [16] as self-heating breakdown and can be interpreted by the damage of the thin film electrode (metal electrode in our MIS structures) in the region of the broken channel. This is not "true" material breakdown of the insulator, because if one further increases voltage, some current will appear again and grow with voltage as shown in Fig.2. Nevertheless the determined breakdown field E_b can be considered as the under-estimated value of the material breakdown.

Fig.3 illustrates annealing effect. Fig.3a shows changes in chemical structure with annealing time.



a)



b)

Figure 3. Effect of isothermal annealing on C-H_x and C=C bondings (a) and on resistivity an dielectric constant (b).

It can be seen that C=C concentration with time $C_{C=C}(t)$ firstly increased and then practically did not change, while C-H concentration $C_{C-H}(t)$ and consequently hydrogen content continuously reduced. The $K(t)$ and $\rho(t)$ behavior correlated with $C_{C=C}(t)$ for the former and with $C_{C-H}(t)$ for the latter. A reduction of resistivity with $C_{C=C}$ could be expected, because graphite like C=C bonding would provide an effective carrier transport. An increase of dielectric constant could be tentatively attributed to densification of material because of hydrogen loss. However, more systematic and detailed research is necessary to improve understanding of relationship between deposition conditions, microstructure and electrical characteristics in low-K carbon films.

4 SUMMARY AND CONCLUSIONS

We have deposited amorphous carbon films under different conditions in low frequency capacitive discharge and studied the structure of C-H and C=C chemical bonding, dielectric constant, resistivity, and breakdown in these films. Effect of annealing on the above characteristics has been also studied. Our observations and data analysis allow us to draw the conclusions as follows:

- Deposition conditions significantly effect on both C–H, C=C microstructure and concentrations of these bondings,
- There is not simple correlation between concentration of C–H, C=C bondings and electrical characteristics; we have found that the best dielectric properties such as high resistivity $\rho \approx 10^{14}$ *Ohm cm*, low dielectric constant $K=2.1$, high breakdown field $E_b=1.5*\ 10^6$ *V/cm*, were observed in the films with the "optimal" concentration of both C-H and C=C bonds,
- At low electric field $E<2.5$ *V/cm* the charge carrier transport is controlled by space charge limited current; at high pre-breakdown electric field the transport mechanism is changed and Schottky type electron emission from the electrode begins to dominate.
- Annealing at $T=400$ *°C* increases C=C and reduces $C\text{-}H_x$ bonding concentrations, while resistivity reduces by about order and dielectric constant increases from $K=2.1$ *to* $K=3.1$. Presumably the former is related to effect of graphite phase and the latter can be attributed to hydrogen loss.

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