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INFLUENCE OF Ar PARTIAL PRESSURE DURING DEPOSITION, ON THE I-V CHARACTERISTICS OF METAL-a-C:H-METAL DEVICES

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Results of electrical measurements of a-C:H films deposited by RF plasma containing methane (CH_4) and several argon partial pressures (p_{Ar}) with $0 \le p_{Ar} \le 80\%$, are presented. The obtained experimental results have shown that for these films, deposited using partial Ar pressure, $p_{Ar}(\%) = p_{Ar}/(p_{Ar}+p_{CH4}) \le 50\%$, the dependence of the density of current (J) on applied voltage (V) is linear (ohmic) and for $p_{Ar} > 50\%$, space charge limited current (SCLC) of injected carriers appears (power dependence $J \sim V^s$ with $s > 1$). The characteristic values of temperature (T_c), in the interval where $s > 1$ (non-ohmic) as a function of p_{Ar}, was found. From visible Raman and FTIR analyses it was shown that the high values of the ratio $\Phi = sp^3/(sp^3+sp^2+sp^1) \cong 55\%$, (in the interval $12 \le p_{Ar} \le 50\%$), are for diamond sp^3, for graphite sp^2 and for carbon, sp^1. The J-V measurements have shown that in the same interval of small p_{Ar} ($12 \le p_{Ar} \le 50\%$), the slope (s) of the straight line logJ= log f(V) is s = 1(ohmic behavior).This may suggest that ohmic behavior obtained for small valued of p_{Ar}, may be connected with high values of Φ. The dependence of the values of value of b (the intersection with log(J) for log(V) = 0) on p_{Ar}, has shown that at large partial Ar pressure ($p_{Ar} \ge 50\%$), abrupt increase of b appears.Since $b \sim \mu$, the increase of b with p_{Ar} (for $p_{Ar} \ge 50\%$) may indicate increase in mobility and as a consequence corresponding decrease of the concentration of localized traps of injected carriers.

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1. Introduction

Diamond-like amorphous a-C:H films have found already very large applications in the fields of protective layers against mechanical and chemical damage, and semiconductor devices (solar cells, switches for active matrix displays) [1-5] Discovery of the low and negative affinity of DLC has lead to development of more sensitive light amplifiers [6]. The a-C:H is obtained mainly by deposition of films from RF plasma of methane (CH_4) [7-9]. In previous experiments, it was shown that the addition of Ar to the methane gas may improve the film properties (e.g., adhesion, density) [10-11], or to decrease the film-substrate stress [10]. One of the first types of devices based on a-C:H films deposited without addition of Ar was published in Ref. 12, where it was shown that non-linear I-V effects may appear in Metal-a-C:H-Metal devices, made of Al-a-C:H-Cu films. Recently, a metal-semiconductor-metal (M-S-M) type of device based on a-C:H films was developed, for pixels of active liquid crystal displays applications], where was shown that the non-linear dependence of density of current (J) on applied bias (V) is of the Poole-Frenkel type [13].

In this paper, we present results obtained on the current-voltage (I-V) characteristics of M-a-C:H-M films deposited on sapphire and glass substrates. The a-C:H films were obtained by deposition from RF plasma of mixed methane and argon (CH_4 + Ar), for several values of the partial pressure of Ar ($p_{Ar}(\%) = p_{Ar} / (p_{Ar}+p_{ch4})$). The measured dependence $J \sim V^s$ is ohmic (s = 1) for low concentrations of p_{Ar}. Non-ohmic characteristic (s > 1), for large values of p_{Ar}, was obtained. Using the results of theoretical studies, [14-19], it was shown that the space charge limited current (SCLC) determines the I-V non-linear characteristics of the M-a-C:H-M devices, in this case. In the paper [18] were studied amorphous diamond-like films using SCLC measurements and the model of Davis and Mott [20] for amorphous materials, and was calculated the density of states (DOS), which consisted of extended and localized states.

2. Experimental

The a-C:H films were deposited, using plasma R.F. (13.56 MHz) glow discharge in a methane gas (CH_4)+Ar [14]. Deposition was made after evacuating the air in the chamber to pressure $p \leq 1.33 \times 10^{-4}$ Pa. Dimensions of the vacuum chamber were the following: diameter of 50cm , height of 80 cm, diameter of electrodes 20 cm and spacing between anode and cathode 8-10cm.The deposition was made using the optimum power of 200 W for which was obtained maximum Φ without Ar ($p_{Ar} = 0$ %). Mass flow controllers (MFC) controlled the ratio of flow rate of gases. The range of Ar partial pressure ($12 \leq p_{Ar} \leq 80$%,), relative to the total constant pressure (6.7×10^{-1} Pa), of CH_4+Ar, was measured using Micropole Analyzer.

The J-V characteristics for the samples were obtained using planar gap-cell structure, consisting of Al contacts with spacing $10 \leq W \leq 1000$ μm, as shown in Fig. 1. The contacts were patterned on the a-C:H films using photolithography. All contact films were deposited, using an ion beam sputtering equipment.

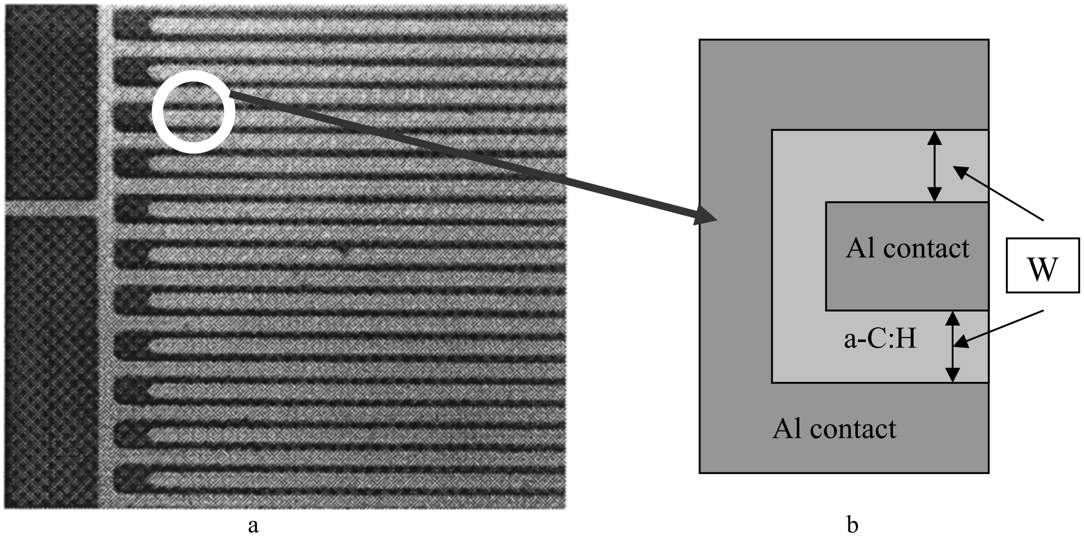

Fig. 1. (a) Top view of the Al electrodes (magnification X40).
(b) Cross-section of electrodes seen in (a).

During a-C:H films deposition, the temperature of the substrate was maintained constant at about 20 ^{0}C, using water cooling of the electrode.

The variation of the current with applied voltage, in the negative and positive direction has not exhibited any polarization (hysteresis). No heating or transient phenomena were observed during the time of applied biases. A Keithley 228 was used for the I-V measurements, which were repeated for several values of the spacing (W) between the contacts ($10 \leq W \leq 1000$ μm). During the process of a-C:H film deposition, the Ar ions may produce partial or total sputtering of the obtained films. For this reason, calibration of the thickness (d) as a function of P_{Ar}, was made using an Alpha step 100 profilometer. In Fig. 2, the dependence of deposition rate D (where d is the thickness and t time of deposition), as a function of P_{Ar} is shown.

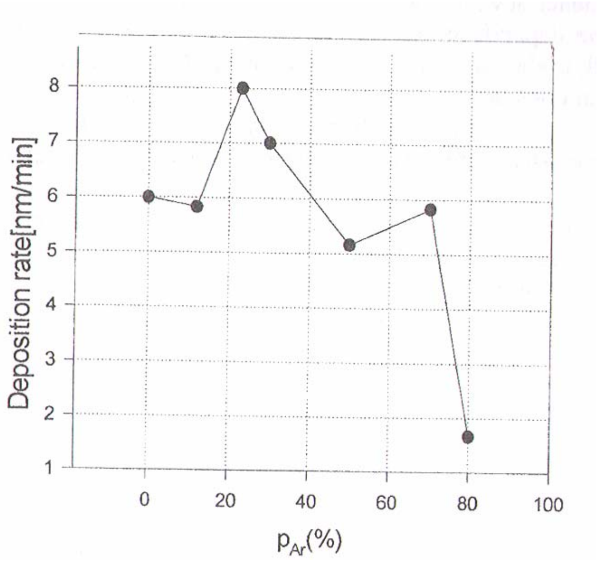

Fig. 2. Dependence of a-C:H deposition rate vs. p_{Ar}, for sapphire substrates.

3. Theoretical considerations, experimental results, and discussion

Taking into account the low conductivity ($\sigma \leq 10^{-9}\Omega^{-1}.cm^{-1}$) of our samples, deposited in partial pressures of P_{Ar} we may consider that SCLC characteristics, may appear by applying voltage. This type of characteristics was studied before and important studies were published by Rose [14], Mott and Gurney [15]. More detailed experimental and theoretical studies made of these phenomena were published, e.g., in [16-19]. Important for understanding the data obtained in our measurements were the theoretical results for SCLC for high resistivity materials with thermal free carriers and fixed space charge, for shallow and deep traps of carriers. These results are suitable for a-C:H layers which is low conductivity amorphous material containing high concentration of traps [18].

For the understanding of the results obtained in our measurements, we shall take into account the theoretical studies of SCLC in Metal-Insulator-Metal (MIM) systems. The essential characteristic of the SCLC, is the non-linear power dependence of the current density (J) on bias voltage (V). The non-linear dependence J(V) is obtained taking into consideration the charge (Q), accommodated in the capacitance formed by the MIM and the transit time (t) between the electrodes. In [14-16] the power relation $J \sim V^s$ of a trap-free insulator with thermal carriers, was obtained

$$J=(9/8)\varepsilon\varepsilon_0\mu\, V^2/W^3, \quad (1)$$

where ε_0 is the permittivity of vacuum, ε the dielectric constant, W the spacing between the electrodes and μ the mobility of the a-C:H film the area of electrodes is unity.

As was shown theoretically [14, 16, 19], for the case of insulators with traps, which may capture the injected carriers, the dependence of J on V will be changed. The relation J(V) will depend on the distribution of traps in the energy gap. For a uniform distribution of traps, the value of J will depend exponentially on the applied voltage [14], which was not observed for our a-C:H samples deposited in p_{Ar}. For step distribution of traps [14] was obtained:

$$n_t \sim \exp(-A/kT_c), \quad (2)$$

where n_t is the concentration of traps, A is the energetic distance of traps to band, k is the Boltzmann constant and T_c is a characteristic temperature which will determine the type of variation with energy. Small values of $T_c < T$ (T is the value of ambient temperature), will give rapid, and large values of T_c, slow variation of n_t as a function of A, respectively. Rapid variation of trap distribution will give a strong decrease of the concentration of deep traps and the remaining shallow levels will correspond a similar square dependence J(V) as was obtained for trap-free case, Eq.(1).

In Fig. 3 the dependence of log (J) on log (V) of our sample p_{Ar}=23, for which a slope s = 1.07 was obtained, is shown, which is almost a linear (ohmic) power dependence of J(V).

The a-C:H samples are amorphous (high density of traps) and if these traps act as trapping centers, the injected carriers will be trapped and no space charge will appear. In this case the concentration of thermally generated equilibrium carriers will determine the ohmic ($J \sim V$) conduction.

In our experiments, for low concentrations of Ar partial pressure ($12 \le p_{Ar} \le 50\%$) we obtained $s \cong 1$ (ohmic characteristics of J-V, see e.g., Fig. 3), which may suggest that in this case when only the thermal equilibrium free carriers (no space charge), determine the conductivity is $\sigma = e\mu n$ (e-charge, μ mobility, and n density of free carriers), which is not a function of the field (E=V/W):

$$J = \sigma V/W \tag{3}$$

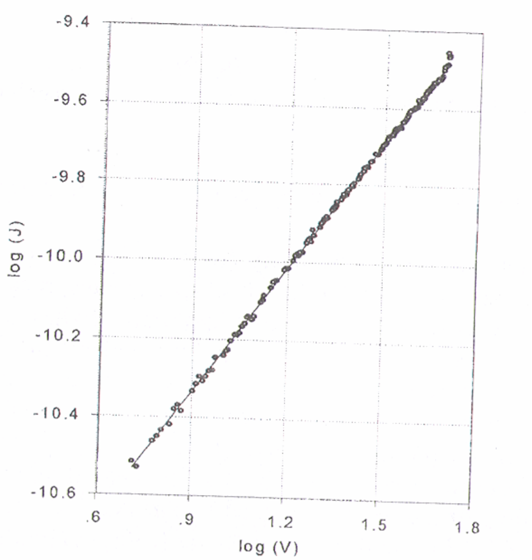

Fig. 3. log (J) vs. log (V) for the sample p_{Ar}=23. Slope of the straight line s=1.07.

In this case the J-V characteristic will be a straight line which may be represented as:

$$\log(J)= s \log (V)+\log (b) \tag{4}$$

where s = 1 and b = σ/W = constant.

For the case of p_{Ar} = 70, and 80%, the value of s is larger than 2.

As shown theoretically in [14,19], for a step distribution of traps (see also Eq.(2)), in the energy gap (decrease of traps concentration of from the extended states band), relation:

$$J = b(V^{(Tc/T)+1})=bV^{s}, \tag{5}$$

was obtained, where for ($T_c > T$) s > 2, and b ~ $(\mu ekn)/W^2$), (k-Boltzmann constant, W-spacing between electrodes, μ-mobility, and n-density of free carriers), constant independent on V.

This corresponds to a power dependence higher than square, for a-C:H samples $p_{A\ r}$= 70 and 80%. In this case the log of Eq(5) has to be a straight line with slope s = $(T_c/T)+1$ and intersection with ordinate for log(V) = 0 of log(J) = b (Eq.(6):

$$\log(J)=s \log(V)+\log b \tag{6}$$

From the values shown in Figs. 4 and 5, the dependence of log(J) on log(V) (straight line), of sample p_{Ar} = 70 and 80%, is represented, as seen a slope s = 2.4 and s = 4.6, obtained respectively.

For the measured J at V = 0.9Volt, a very small value of $J = 6 \times 10^{-11}$ and $J = 2.9 \times 10^{-10}$ A is obtained for samples p_{Ar} = 70 and 80, respectively. This gives another argument in the favor of the hypothesis that those samples may be insulators and may give SCLC behavior. From the slope $s = [(T_c/T)+1]$ obtained in Figs. 4 and 5 and using Eq.(6), for T = 300 K, is obtained T_c 420 and 1077 K for the sample p_{Ar}=70 and p_{Ar} = 80%, respectively.

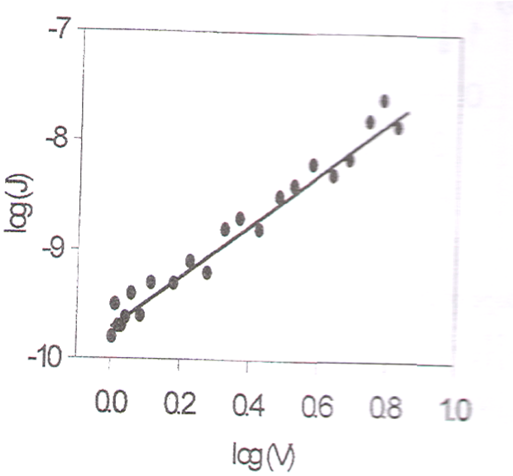

Fig. 4 log(J) vs. log(V) for sample p_{Ar}=70, measured (●●●) and calculated (──) data.

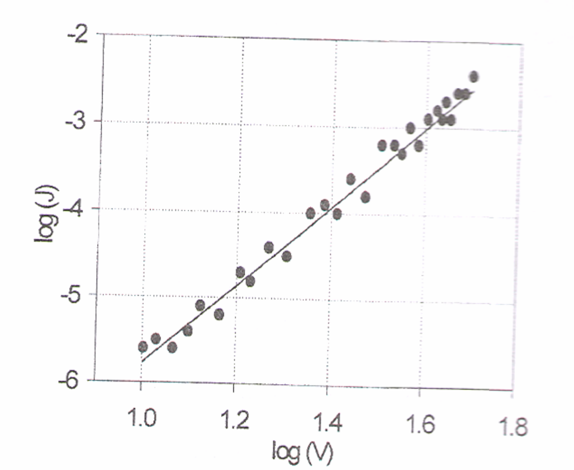

Fig. 5 log(J) vs. log(V) for sample p_{Ar}=80, measured (●●●) and calculated (──) data.

In Fig. 6, the dependence of the value of slope s as a function of Ar partial pressure $12 \leq p_{Ar} \leq 80\%$, is shown. For $12 \leq p_{Ar} \leq 50\%$, s is about 1, practically constant (ohmic behavior) for the three samples with p_{Ar} = 12, 23, 30 and 50%. and for x = 70 and 80**,** an abrupt change (> than four times), occurs.

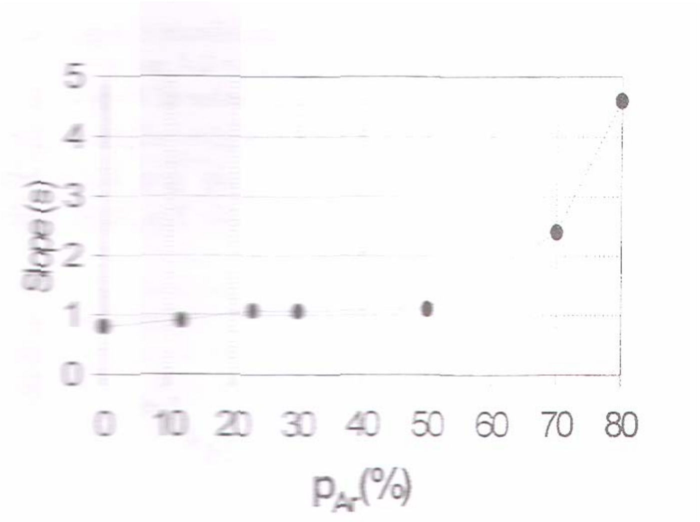

Fig. 6. Slope of the straight line from Eq.(6) vs. p_{Ar}, for all a-C:H samples.

As seen from FTIR and visible Raman (Fig. 7), samples deposited at partial pressure $12 \le p_{Ar} \le 50$, gave much larger Φ ratio than for $p_{Ar} > 50\%$. and practically constant.

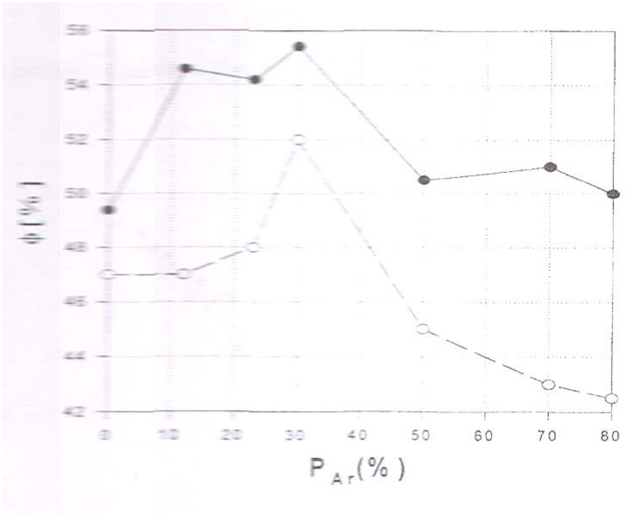

Fig. 7. Ratio Φ vs. Ar partial pressure (x), measured by FTIR(──) and Raman (-----).

This may indicate that Φ, for samples deposited at p_{Ar} where the samples show ohmic behavior (s = 1) is larger than for those where s > 1 (non-linear *J-V* characteristics). Taking into consideration that log *J*(*V*) is a straight line and from data shown in Figs. 4 and 5 and Eq(6), we obtained the values of log(b). The value of b for $p_{Ar} = 70$ was $b = 2.3 \times 10^{-10}$ and for $p_{Ar} = 80$, $b = 3.7 \times 10^{-9}$. In Fig. 8, the dependence of b on p_{Ar} is shown where it is seen that for $12 \le p_{Ar} \le 50\%$ the value of b increases slowly and for $p_{Ar} > 50\%$ an abrupt increase appears.

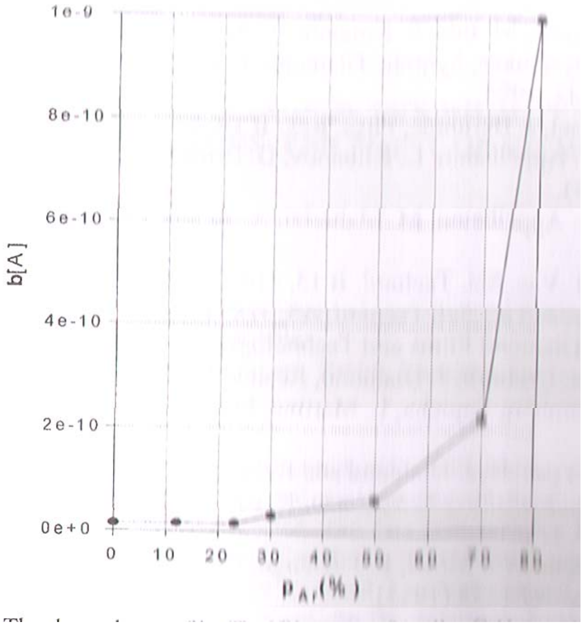

Fig. 8. The dependence of b (Eq.(6)) vs. p_{Ar}, for all a-C:H samples.

Since s > 2 (see Fig. 6) for $p_{Ar} = 70$ and 80%, and we assume that Eq.(4) may be applied in this case [14], the value of b will be proportional to μ. (Eq.(5)).

Taking into account that a-C:H is an amorphous material which contains high concentration of traps into the energy gap, an increase of b which corresponds to increase of μ, will be due to a reduction of traps which contribute to capture of injected carriers and in this case the value of σ is determined not only by equilibrium thermal but also by injected (SCLC) carriers which will increase the conductivity in comparison to that of the samples deposited at $p_{Ar} \leq 50\%$. This was experimentally observed in the J-V characteristics in Figs. 4 and 5 for p_{Ar} of 70 and 80%, respectively where $\sigma = 3.7 \times 10^8$ For $p_{Ar} = 70\%$ and $\sigma = 3.4 \times 10^8$for $p_{Ar} = 80\%$ in comparison to sample $p_A = 23\%$, where $\sigma = 1.4 \times 10^9$ These values of σ are larger than those obtained for $p_{Ar} \leq 50\%$, where the concentration of traps which acted as recombination centers has prevented the injected carriers from participating in the conduction and σ is given only be the thermal equilibrium free carriers. From the FTIR, Raman and XPS analysis, was shown that Φ is larger for the samples obtained by $p \leq 50\%$, which leads to the conclusion that a-C:H films deposited at low p_{Ar} have larger concentration of traps (high trapping of injected carriers, which gives low σ) and higher Φ, and the increase of p_{Ar} reduce the concentration of traps (less trapping, which gives higher σ) and lower Φ. The lower value of Φ is an indication of increase of graphite and amorphous carbon bonds in the samples, which may be due to the high partial pressure of argon during deposition.

4. Conclusions

The samples deposited at Ar partial pressures ($12 \leq p_{Ar} \leq 50\%$) have shown ohmic behavior $J \sim V$. Measurements of FTIR, Raman and XPS have indicated that high ratio of the $\Phi = sp^3/(sp^3+sp^2+sp^1)$ bonds appear for $12 \leq p_{Ar} \leq 50\%$,where $54 \leq \Phi \leq 57\%$. Space charge limited current (SCLC) of injected carriers appear for $p_{Ar} = 70$ and 80% and for these samples the values of the characteristic temperature T_c, were calculated. The increase of p_{Ar} during deposition reduces the value of Φ and increase σ.

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