Bull. Mater. Sci., Vol. 33, No. 3, June 2010, pp. 215–220. © Indian Academy of Sciences.

Electron field emission from sp^2-induced insulating to metallic behaviour of amorphous carbon (*a*-C) films

PITAMBER MAHANANDIA*, P N VISWAKARMA, PRASAD VISHNU BHOTLA, S V SUBRAMANYAM and KARUNA KAR NANDA[†]
Department of Physics, [†]Materials Research Centre, Indian Institute of Science, Bangalore 560 012, India

MS received 20 October 2010

Abstract. **The influence of concentration and size of sp^2 cluster on the transport properties and electron field emissions of amorphous carbon films have been investigated. The observed insulating to metallic behaviour from reduced activation energy derived from transport measurement and threshold field for electron emission of *a*-C films can be explained in terms of improvements in the connectivity between sp^2 clusters. The connectivity is resulted by the cluster concentration and size. The concentration and size of sp^2 content cluster is regulated by the coalescence of carbon globules into clusters, which evolves with deposition conditions.**

Keywords. **Amorphous carbon; transport; field emission.**

1. Introduction

Amorphous carbon (*a*-C) and hydrogenated amorphous carbon (*a*-C : H) which consist of sp^2 and sp^3 hybridized phases have attracted considerable attention due to the possible applications as semiconductor materials (Silva *et al* 1998) and as potential field emission cathode materials (Jaskie 1996). The transport properties and the electron field emission are highly influenced by the sp^2 content cluster size in the sp^3 matrix. There are ways to study the effect of sp^2 cluster size, such as by varying deposition conditions (Lifshitz *et al* 1989), post treatment (Raiko *et al* 1996; Hart *et al* 1999; Mao *et al* 1999; Lin *et al* 2000), by thermal annealing (Robertson 1991; Burden *et al* 1999) and local heating (Prawer *et al* 1987; McCulloch *et al* 1995). In some cases, incorporation of nitrogen into *a*-C films has also introduced larger sp^2 content clusters, leading to a change in transport and electron field emission properties (Hoffman and Gaerttner 1980; Llie *et al* 2000; Satyanarayana *et al* 2000). Though post treatment and annealing results in higher sp^2 content cluster sizes, graphitization of the sample has been observed. However, the exact mechanism of improved quality is not clear because of amorphous phase and crystalline graphite phase present in *a*-C films.

In this paper, we report the morphological evolution and influence on their transport and field emission properties of *a*-C films. The *a*-C films are not treated aftermath of their preparation and furthermore no macroscopic graphitization is observed on as synthesized samples. It is observed that coalescence of carbon globules results in clustering, increases the sp^2 phases and improves the conductivity as well as the field emission behaviour of the *a*-C films. This gives a direct evidence of the correlation between sp^2 contents, conductivity and field emission properties of *a*-C films. Reduced activation energy derived from the transport measurement indicates that the nature of the carbon films can be switched from insulating to metallic by increasing the sp^2 content. It is also seen that the threshold field of the *a*-C films derived from the field emission measurement is lowered for higher sp^2 content.

2. Experimental

The samples were prepared by a simple pyrolysis method at different temperatures (700, 800 and 900°C) (figure 1) and characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Raman spectroscopy. Amorphous carbon films were prepared from $C_4H_2O_3$ (maleic anhydride) and taken in a length of 50 cm and 1 cm inner diameter quartz tube closed at one end. Quartz substrate (size $5 \times 5 \times 1$ mm) ultrasonically cleaned in water followed by acetone was positioned at the centre of first zone furnace inside the quartz tube. The open end of the tube was closed with a rubber bladder. The quartz tube was evacuated and purged with argon gas prior to pyrolysis. The pyrolysis process was performed for 3 h and 30 min and then the furnace was switched off and allowed to cool under normal ambient conditions. The residual gas consisting of mainly CO or CO_2 was collected in the rubber bladder. Following this process, samples were prepared at 700, 800, and 900°C by pyrolysis

*Author for correspondence (pitam@physics.iisc.ernet.in)

assisted CVD in argon atmosphere using two-zone furnace arrangement. About 120 mg of the carbon precursor maleic anhydride was taken. The amorphous nature of the films was characterized by XRD, which shows the broad hump centred at ~22° confirming amorphous nature of the carbon (figures 2a–c). The surface morphology of different samples was investigated by SEM and is shown in figures 3(a)–(c). We observed that the *a*-C films prepared at 700°C were made up of spherical globules with an average size of 1–2 μm, whereas the globules coalesced to form clusters for *a*-C films prepared at higher temperature, 900°C and was noticed to be increasing in size and numbers. The cluster islands were seen clearly in the SEM images. Raman spectroscopy was mainly sensitive to sp^2 sites and was a convenient way to follow the evolution of sp^2 phase. The Raman spectra are shown in figure 4. The *D* and *G* peaks appeared at 1347 cm^{-1} and 1578 cm^{-1} with nearly the same intensity for carbon globules of *a*-C film prepared at 700°C (figure 4(a)). But for the sample prepared at 900°C, *a*-C films, the *D* and *G* peaks appeared with different intensities (figure 4(b)). The I_D/I_G ratio was used to estimate the sp^2 clusters size. I_D/I_G values decreased with increasing cluster size (Tamor *et al* 1989; Tang *et al* 1993). The I_D/I_G value changed from 1–0·7 indicating higher clustering of the sp^2 phases (Ferrari and Robertson 2000; Casiraghi *et al* 2000) and was evident from the XRD and SEM characterization also. The surface morphology of the *a*-C films was studied by Vishwakarma *et al* (2005). It is reported that when *a*-C films are prepared at temperature 700–900°C, nucleation of well defined islands start, which are not very prominent at 700°C but more prominent at 900°C. Probably these sp^2 content cluster islands are good emersion sites.

3. Results and discussion

The sp^2 sites control the electronic and transport properties in *a*-C films, because their π states lie around the optical bandgap region. According to Carey and Silva (2004), the sp^2 hybridized carbon atoms tend to exist in clusters in the form of graphitic rings or olephinic chains giving rise to π and π^* bands, which lie largely within the gap of σ–σ^* bands. The location of the sp^2 clusters in the energy gap depends on two factors: whether they consist of even or odd numbers of carbon atoms and whether they are distorted. Undistorted even numbered clusters will give rise to states near the Fermi level (E_F) only if they are sufficiently large. This differs from the case of odd numbered clusters, which can give rise to gap states even if composed of a small number of atoms. In general, distorted clusters give rise to states that are closer to E_F than undistorted clusters. The consequent overlap of the clusters results in electron delocalization and/or enhanced hopping conduction mechanism between the clusters (Dasgupta *et al* 1991). This is regarded as an effective improvement in the connectivity between the clusters. Transport measurements were carried out on these films making four-point contacts in the temperature range 1·2–300 K and the logarithmic plot of resistivity as a function of temperature is shown in figures 5a–c. The resistivity is high for the *a*-C film with low sp^2 content (*a*-C film prepared at 700°C), whereas resistivity is found to decrease for the higher sp^2 content *a*-C films (*a*-C prepared at 900°C). At higher preparation temperature, the concentration of sp^2 content clusters and cluster size increases. This results in providing better connectivity between the clusters. Hence, the hopping distance decreases for the higher sp^2 content clusters thereby decreasing the resistivity (Khan *et al* 2001). The reduced activation energy (Menon *et al* 1993) (*W*) plot shows insulating to metallic behaviour as shown in the inset of figure 6. The sp^2 content cluster size, which provides better connectivity in the *a*-C films are responsible for the transition from insulating

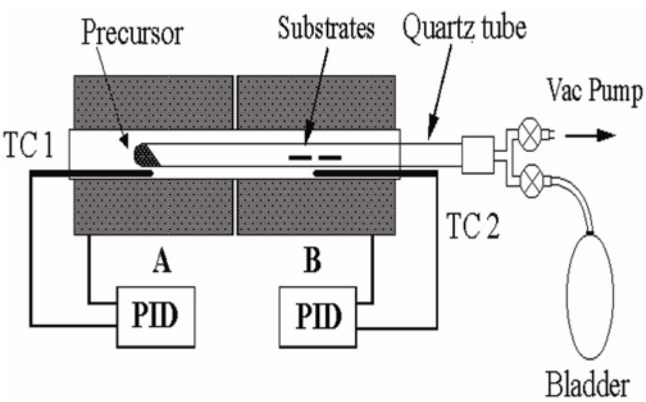

Figure 1. Double zone pyrolysis setup.

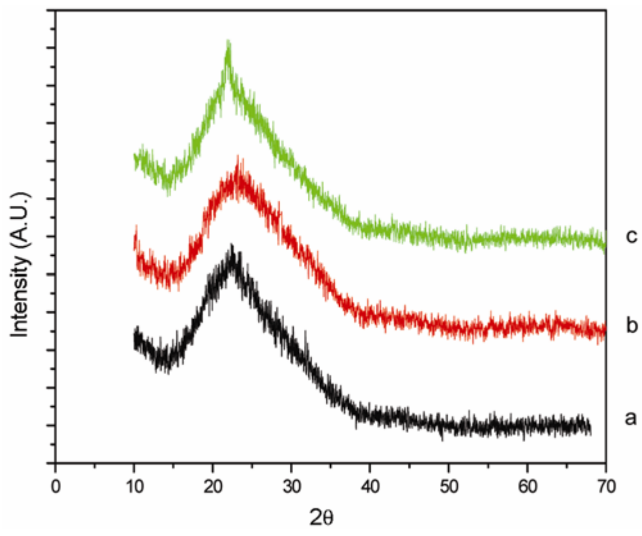

Figure 2. XRD pattern of *a*-C films prepared at (a) 700°C, (b) 800°C and (c) 900°C.

to metallic behaviour. The delocalization of electrons near Fermi level also has potential impact on field emissions (Carey *et al* 2000). Electron field emission was studied and the influence of sp^2 content in the *a*-C films was investigated. The cleaned amorphous carbon thin films deposited on quartz substrate (size 5 × 5 × 1 mm) were mounted on a copper plate of 10 mm in diameter and thickness, 1 mm. Silver paste was used to mount the substrate onto the copper plate to ensure good contact between substrate and plate. The amorphous carbon thin film on the substrate that acts as a cathode mounted on copper plate sits on the platform of the emission unit. Gold plated tip of 0·2 mm diameter has been used as anode. The emission current is derived by measuring the voltage across the 500 kΩ resistor applying the voltage to the anode in step of 20 V from 0–1400 V in a vacuum of

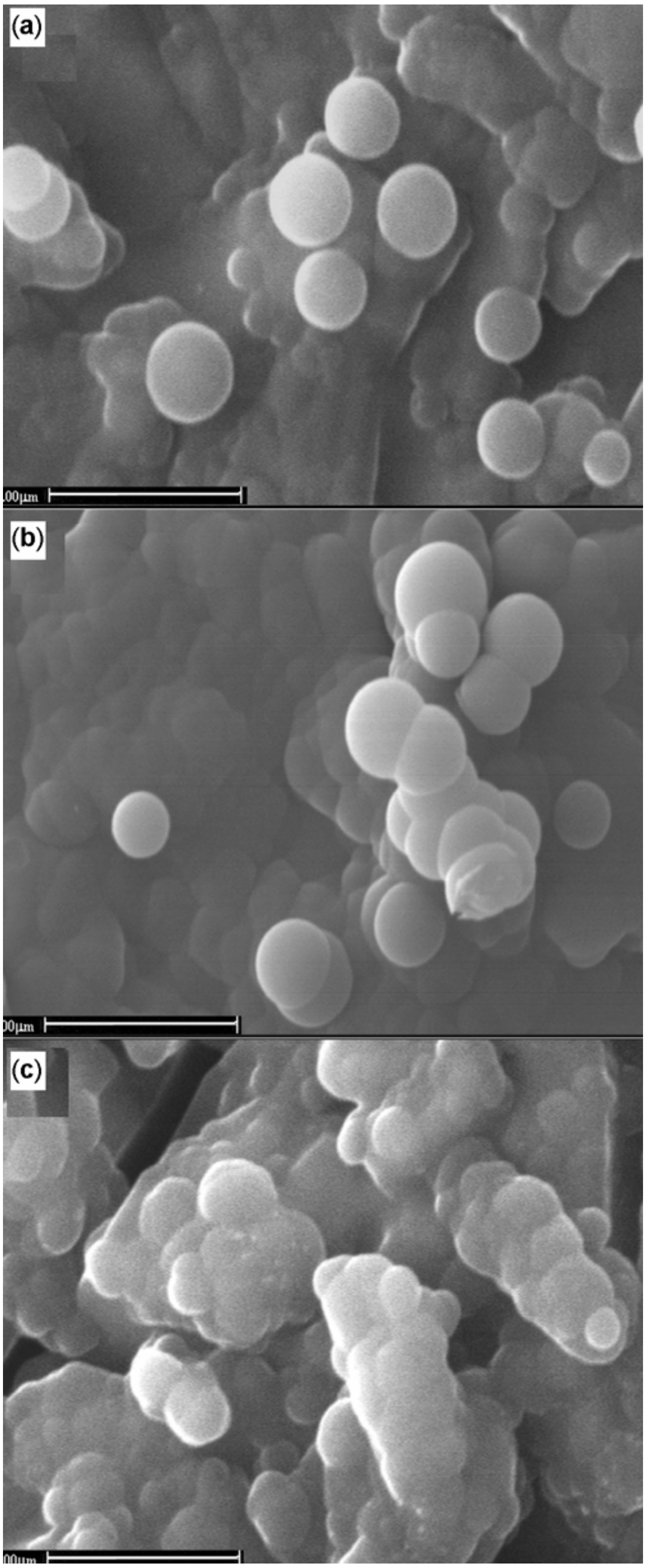

Figure 3. SEM images of *a*-C films prepared at (**a**) 700°C, (**b**) 800°C and (**c**) 900°C.

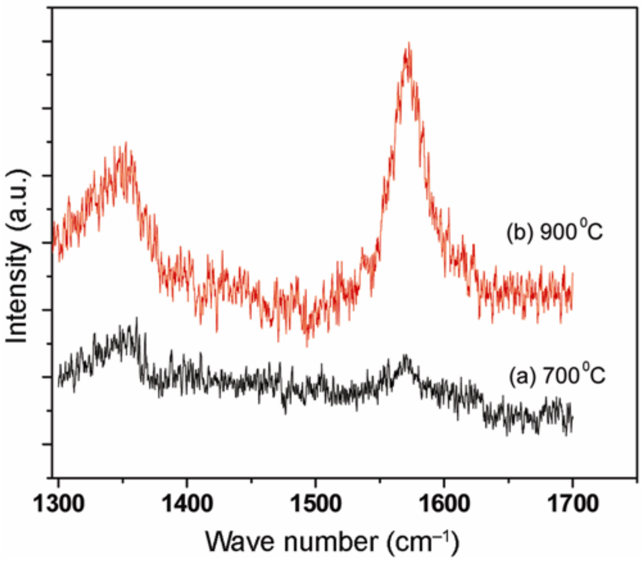

Figure 4. Raman spectra of *a*-C films prepared at (a) 700°C and (b) 900°C.

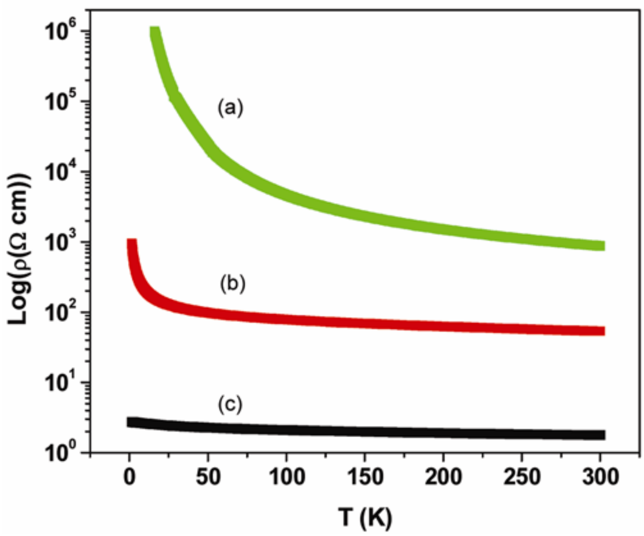

Figure 5. (a) Resistivity plot with respect to temperature for the *a*-C films prepared at (a) 700°C, (b) 800°C and (c) 900°C.

1×10^{-6} torr. The cathode to anode distance is 150 μm, which remains constant throughout while changing the voltage (figure 7). The films prepared at higher temperature will have comparatively high sp^2 content, and the consequent overlap of the clusters will result in the connectivity between the clusters. The *a*-C films prepared at higher temperature introduces large number of sp^2 content clusters and the size of the clusters was noticed to be increasing. Application of external electric field will result in local field enhancement around the sp^2 content clusters and will aid in the emission of electrons. Replenishment of the emitted electrons to the surface layer is easily accomplished due to good connectivity between the clusters (Forrest *et al* 1998). This is very clear from the *I–V* plot where emission current is plotted vs applied field as shown in figure 8. The emission current is considerably more for the higher sp^2 content (*a*-C film prepared at 900°C) than the lower sp^2 content samples (*a*-C film prepared at 700°C). The classical explanation for electron field emission from a surface is Fowler–Nordheim (FN) tunneling behaviour. The Fowler–Nordheim emission current equation is as follows:

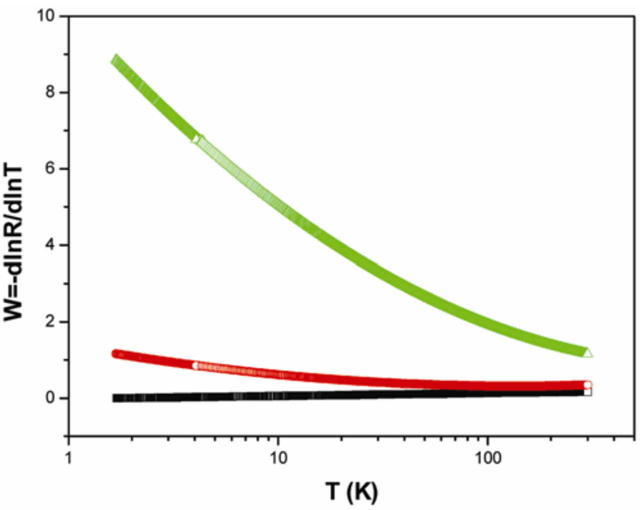

Figure 6. Respective reduced activation energy plots with respect to temperature.

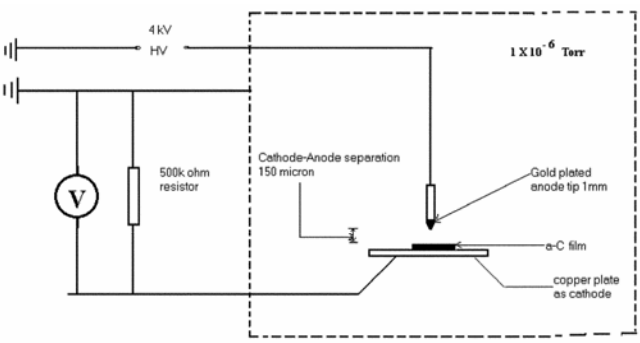

Figure 7. Schematic diagram of electron field emission setup.

$$I = AV^2\beta^2/\phi \exp(-B\phi^{3/2}/\beta V),$$

where I is the emission current (A), V the applied voltage, β the enhancement factor (for flat cathode, $\beta = 1$), ϕ the work function (eV), the numerical constants $A = 1{\cdot}54 \times 10^{-6}$ AeVV^{-2} and $B = 6{\cdot}87 \times 10^{9}$ $(\text{VeV}^{-3/2}\text{m}^{-1})$.

The threshold field has been defined when the steady-state emission current of 1nA is achieved. The threshold fields for the *a*-C films prepared at temperatures of 700–900°C is 4 V/μm, 1·9 V/μm and 1·5 V/μm, respectively. This threshold field value is in agreement with the result reported by Satyanarayana *et al* (1997) for the field emission of tetrahedral amorphous carbon. Kiyota *et al* (1999) obtained as low as 1·2 V/μm threshold field in their field emission study from diamond like carbon (DLC) films. They claim that the threshold field is the lowest among the undoped diamond and DLC films ever reported. We regard this lower threshold field to good connectivity exhibited by higher sp^2 content clusters and their sizes, whereas poor connectivity shows higher threshold field since the sp^2 content cluster is not enough (Carey *et al* 2000).

Field enhancement by a freestanding protrusion of length, l and diameter, r, was reported to be approximated as l/r (Brodie and Schwoebel 1994). Since the l and r values of the present *a*-C films were measured to be of the same magnitude from the surface morphology, the geometric β value was estimated to be of the order of unity. Therefore, the work function, ϕ, of the samples can be evaluated from the $\phi^{3/2}/\beta$ values if we assume an ideal plane emitter with a field enhancement factor, β, of one. The average work function, ϕ, is calculated to be 0·053 eV when we assume $\beta = 1$ in the range of emission current 10^{-8}–10^{-9} A from the slope of the FN plots. Based on the existing mechanisms of electron field emission, it is reported that the work functions of *a*-C and *a*-C : H are

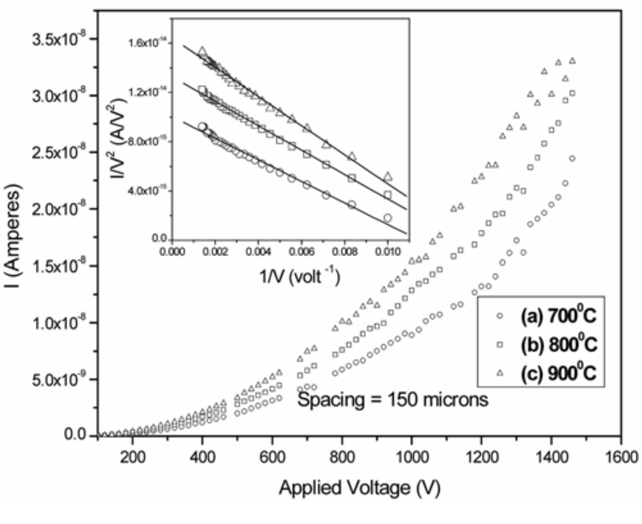

Figure 8. The *I–V* and the FN (I/V^2) vs $1/V$ plot is shown in the inset.

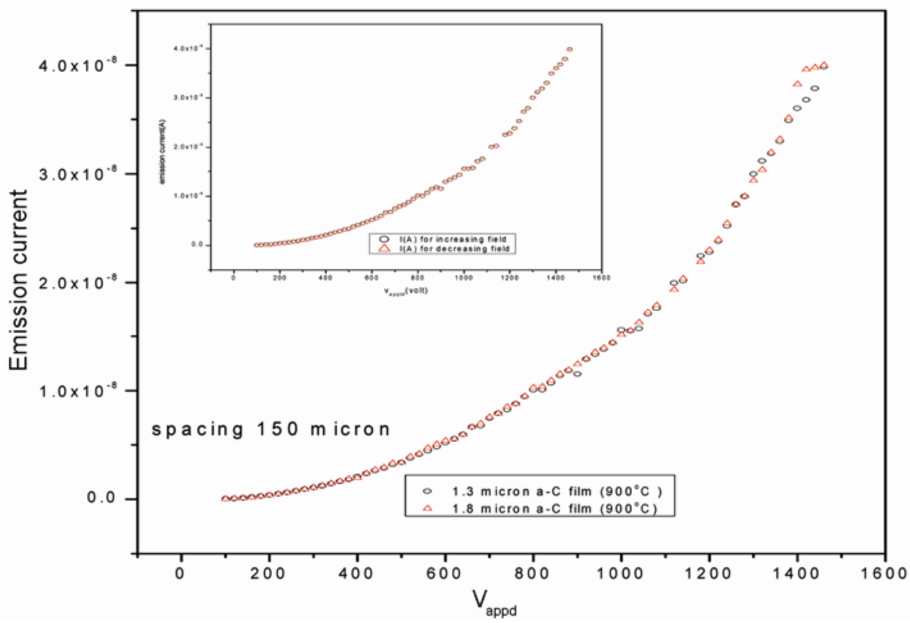

Figure 9. *I–V* plot of *a*-C film of thickness, 1·3 μm and 1·8 μm and the inset is the *I–V* plot of increasing and decreasing applied fields.

estimated in the order of 3·5–4·0 eV (Robertson 1999), while that of the diamond with graphitic patches is 3–4·2 eV (Cui and Robertson 2002) depending on whether the surface is hydrogenated. However, in the case of nitrogenated diamond, *a*-C : H : N and *a*-C : N, extremely low work functions, ~0·01–1·0 eV, have been observed (Bandis and Pate 1996; Silva *et al* 1997; Zhu *et al* 1998; Fan *et al* 1999; Robertson 1999; Badi *et al* 2000; Zheng *et al* 2003).

Photoelectron measurements, however, suggest that work functions of *a*-C films are 3·5–4·0 eV when the bandgap is approximately 2 eV (Ristein *et al* 1995). This value conflicts with the small work function of 0·053 eV obtained in the present study. Therefore, the enhancement factor, β, needs to be clarified for the origin of low threshold emission from *a*-C films. The field-enhancement factor can be calculated from the slope if the work function of the emitter is known. By assuming that $\phi = 4$ eV, the enhancement factor, β, is calculated to be 1120–1370. Such large enhancement values are usually obtained for carbon nanotubes (Chhowalla *et al* 2001). It is reasonable that carbon nanotubes show large enhancement factor because of the high aspect ratio and small radius (large (l/r) value). Kiyota *et al* (1999) also obtained a large value of β in their field emission study from DLC films deposited by electrolysis of methanol liquid. They argue that the nanometer sp^2 cluster sizes (1·5 nm or less), which are equivalent to the diameter of a single walled carbon nanotube are responsible for the strong field enhancement value. However, in the present case, we attribute the crowding microsize sp^2 clusters islands for the large enhancement value. Moreover, the enhancement factor of *a*-C films, which have homogeneous surfaces, must be affected not only by the surface geometry, but also by the internal structures of the films. The investigation of field emission from *a*-C or doped/treated *a*-C films by different groups including the present study reveals that the observed values of different emission currents, work functions, enhancement factors, and threshold fields depend upon the sample preparation conditions by different methods.

The Fowler–Nordheim plots of (I/V^2) vs $1/V$ of these *a*-C films show linear slopes and is shown in inset of figure 8. This indicates that the electron tunneling may be the probable mechanism. We believe that higher emission current and reduced threshold field can be achieved at higher vacuum for field emission. Earlier there has been a report which shows the threshold field depending on films thickness (Forrest *et al* 1998). We studied the field emission of the samples of different thicknesses (1·3 μm and 1·8 μm, measured by ellipsometry) prepared at 900°C. However, we observe no change in the behaviour of current vs applied field characteristics (figure 9). Emission from these sp^2-rich films would be characterized as a 'front surface' type emission since the sp^2 clusters are located near E_F. Moreover, we have observed no difference when the field is increased or decreased as shown in the inset of figure 8. After field emission, SEM was taken for the samples. No damage on the emission surface was observed.

4. Conclusions

In conclusion, we have shown experimentally that the conductivity and field emission properties of *a*-C films depend on the connectivity of sp^2 content clusters. The enhanced behaviour of a-C films is due to the increase in sp^2 content which forms clusters giving states near the Fermi level (E_F) which eventually results in electron delocalization, hence increasing conductivity. The insulating to metallic behaviour of a-C films has been explained by experimental verification. Through this present work it is proved that the conductivity as well as field emission characteristics of the amorphous carbon varies with sp^2 content, which essentially means that we could prepare these carbon films to suit for different applications. The enhancement factors were estimated to be 1120–1370 to explain the mechanism of low threshold field emission, by assuming the barrier height as $\phi = 4$ eV. Such large enhancement factors, which are comparable to those of carbon nanotubes, are attributed to the local field enhancement around sp^2 clusters that result from the sp^2 clusters islands, surface geometry, and internal structures of the films. Based on the application needs, a-C can be implemented for possible conducting as well as potential field emission cathode materials.

Acknowledgement

The authors thank the Council of Scientific and Industrial Research, Government of India, for financial support.

References

Badi N, Bensaoula A, Ageev V, Karabutov A, Ugarov M and Loubnin E 2000 *J. Appl. Phys.* **12** 7351

Bandis C and Pate B 1996 *Appl. Phys. Lett.* **69** 366

Brodie I and Schwoebel P R 1994 *Proc. IEEE* **7** 1006

Burden A P, Forrest R D and Silva S R P 1999 *Thin Solid Films* **337** 257

Carey J D and Silva S R P 2004 *Phys. Rev.* **B70** 235417

Carey J D, Forrest R D, Khan R U A and Silva S R P 2000 *Appl. Phys. Lett.* **77** 2006

Casiraghi C, Ferrari A C and Robertson J 2005 *Phys. Rev.* **B72** 085401

Chhowalla M, Ducati C, Rupesinghe N L, Teo K B K and Amaratunga G A J 2001 *Appl. Phys. Lett.* **79** 2079

Cui J B and Robertson J 2002 *J. Vac. Sci. Technol.* **B20** 238

Dasgupta D, Demichelis F and Tagiaferro A 1991 *Philos. Mag.* **B63** 1255

Fan S, Chapline M G, Franklin N R, Tombler T W, Cassell A M and Dai H 1999 *Science* **283** 512

Ferrari A C and Robertson J 2000 *Phys. Rev.* **B61** 14095

Forrest R D, Burden A P and Silva S R P 1998 *Appl. Phys. Lett.* **73** 3784

Hart A, Satyanarayana B S, Milne W I and Robertson J 1999 *Diamond Relat. Mater.* **8** 809

Hoffman D W and Gaerttner M R 1980 *J. Vac. Sci. Technol.* **17** 425

Jaskie J E 1996 *MRS Bull.* **21** 59

Kiyota H *et al* 1999 *Appl. Phys. Lett.* **75** 2331

Khan R U A, Carey J D and Silva S R P 2001 *Phys. Rev.* **B63** 121201

Lifshitz Y, Kasi S R and Rabalais J W 1989 *Phys. Rev. Lett.* **62** 1290

Lin I N, Chen Y -H and Cheng H -F 2000 *Diamond Relat. Mater.* **9** 1574

Llie A, Hart A, Flewitt A J, Robertson J and Milne W I 2000 *J. Appl. Phys.* **88** 6002

Mao D S *et al* 1999 *Mater. Lett.* **41** 117

McCulloch D G, Gerstner E G, McKenzie D R, Prawer S and Kallish R 1995 *Phys. Rev.* **B52** 850

Menon R, Yoon C O, Moses D, Cao Y and Heeger A J 1993 *Phys. Rev.* **B48** 17685

Prawer S, Kalish R, Adel M E and Richter V 1987 *J. Appl. Phys.* **61** 4429

Raiko V, Spitzl R, Aschermann B, Theirich D, Engemann J, Pupeter N, Habermann T and Mueller G 1996 *Thin Solid Films* **290** 190

Ristein J, Schäfer J and Ley L 1995 *Diamond Relat. Mater.* **4** 508

Robertson J 1991 *Prog. Solid State Chem.* **21** 199

Robertson J 1999 *J. Vac. Sci. Technol.* **B17** 659

Satyanarayana B S, Hart A, Milne W I and Robertson J 1997 *Appl. Phys. Lett.* **71** 1430

Satyanarayana B S, Robertson J and Milne W I 2000 *J. Appl. Phys.* **87** 3126

Silva S R P, Amaratunga G A J and Barnes J R 1997 *Appl. Phys. Lett.* **71** 1477

Silva S R P, Robertson J, Milne W I and Amaratunga G A J (eds) 1998 *Amorphous carbon: State of the art, Proceedings of the first international specialist meeting on amorphous carbon* (Singapore: World Scientific)

Tamor M A, Haire J A, Wu C H and Hass K C 1989 *Appl. Phys. Lett.* **54** 123

Tang X M, Weber J, Baer Y, Muller C, Hanni W and Hintermann H E 1993 *Phys. Rev.* **B48** 10124

Vishwakarma P N, Prasad V, Subramanyam S V and Ganeshan V 2005 *Bull. Mater. Sci.* **28** 609

Zheng W T, Li J J, Wang X, Li X T, Jin Z S, Tay B K and Sun C Q 2003 *J. Appl. Phys.* **94** 2741

Zhu W, Kochanski G P and Jin S 1998 *Science* **282** 1471