

UCRL-JC-134674

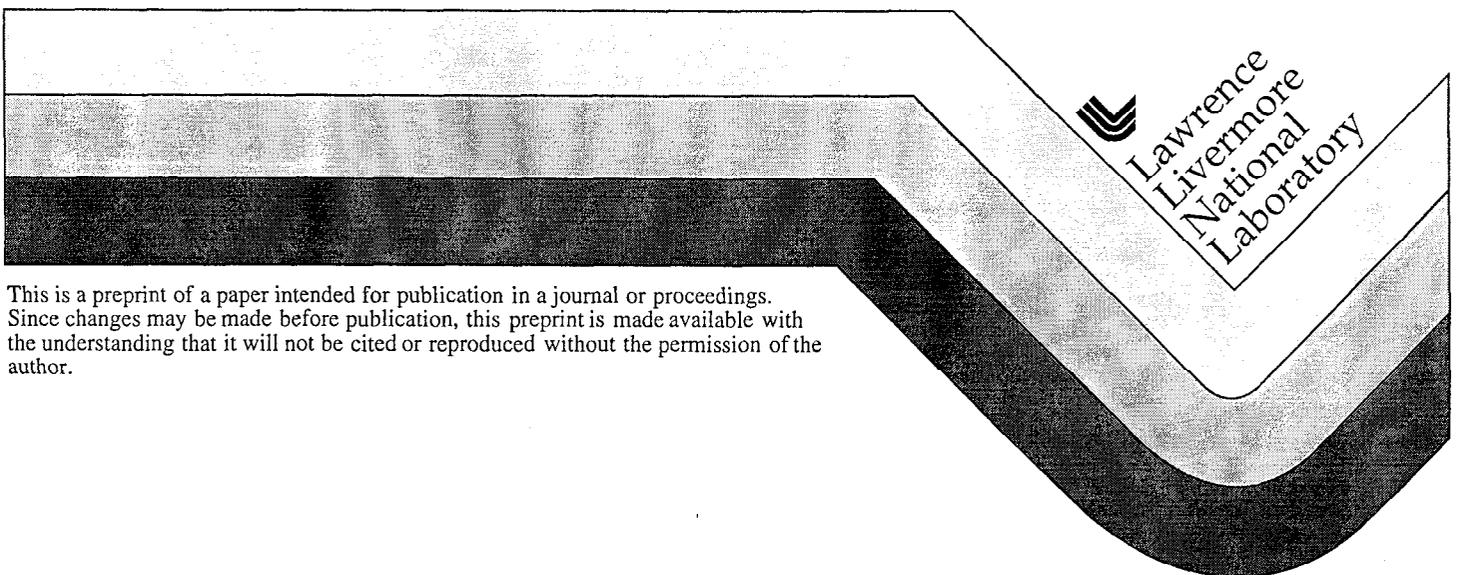
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This paper was prepared for submittal to the  
Materials Research Society 1999 Spring Meeting  
San Francisco, CA  
April 5-9, 1999

April 1999



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## FIELD EMISSION FROM CARBON FILMS DEPOSITED BY VHF CVD ON DIFFERENT SUBSTRATES.

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### ABSTRACT

As previously demonstrated, non-diamond carbon (NDC) films deposited at low temperatures 200-300 °C on silicon tips reduced the threshold of field emission. In this paper we will present the results of the study of field emission from flat NDC films prepared by VHF CVD. Emission measurements were performed in a diode configuration at approximately  $10^{-10}$  Torr. NDC films were deposited on ceramic and on c-Si substrates sputter coated with layers of Ti, Cu, Ni and Pt. The back contact material influences the emission characteristics but not as a direct correlation to work function. A model of field emission from metal-NDC film structures will be discussed.

### INTRODUCTION

The mechanism of enhanced electron field emission in CVD diamond and diamond like carbon (DLC) films remains unclear. Low or negative electron affinity (NEA) has been proven for such films [1] and is widely conjectured to be important for their field emission, but this hardly explains recent experimental evidence that electrons are emitted easily even from graphite. In diamond, as observed by Geis et al. [2], the main barrier controlling emission is at the back contact. In DLC films, however, the principal barrier to electron emission is at the front surface [3]. Back contacts were also discussed in ref. [4]. In tetrahedrally bonded amorphous carbon (ta-C), no direct dependence of field emission on work function of the back contact material was observed [5]. In our previous studies [6,7] we observed a significant effect of pre-growth treatment of the back contact on electron field emission from both silicon tips coated by NDC and from flat NDC films. This suggests that the interface between the back contact and the NDC film is important. Thus, the role of the back contact is controversial and seems to depend on the type of sample. This precludes a universal model for the various carbon films.

In this paper we have studied the effect of back contact material on field emission from a particular type of amorphous non-diamond carbon films ( $a\text{-CH}_x$ ) prepared by very high frequency CVD (VHF CVD) at relatively low temperatures ( $< 250$  °C). These films were simultaneously deposited on various substrates of mono-crystalline silicon (Si) and ceramic (Sital) coated by metals of different work function. Si-C films are also briefly described.

### EXPERIMENTAL

Carbon films were grown at 2 Angstroms per second by VHF CVD using 7%  $\text{C}_6\text{H}_{14}$  + 93%  $\text{H}_2$  at a pressure of 56 mTorr and a flow of 27 sccm. The loaded power density of the discharge was  $0.14 \text{ W/cm}^3$  at 56 MHz. The substrates were p- and n-type silicon and Sital coated by metal

layers. The thickness of the carbon films was about  $d = 1 \mu\text{m}$  and controlled *in situ* by laser interferometry. Pre-growth treatment involved exposure to hydrogen plasma followed by bias enhanced nucleation in 7%  $\text{C}_6\text{H}_{14}$  + 93%  $\text{H}_2$  plasma. Metal layers of  $0.2 \mu\text{m}$  thickness were prepared by DC sputtering from elements of various work function (Ti, Cu, Ni, or Pt). Carbon films were simultaneously deposited on different substrates. Films were characterized by SEM, AFM, AES, and EELS. The latter two techniques rule out significant diamond content in these films. In particular, the C KLL peak at 273 eV is shifted from graphite (270 eV) in the opposite direction of diamond. EELS in the K-level ionization regime (280-296 eV) and in the valence band and plasmon excitation regime (5-40 eV) showed no diamond character.

Field emission was performed at  $10^{-10}$  Torr in a diode configuration using a  $45 \mu\text{m}$  spacer and  $1 \text{ cm}^2$  samples. Emission current,  $I$ , was collected in a window of area  $A = 2 \times 5 \text{ mm}^2$  giving a current density,  $J = I/A$ . Electric field,  $E$ , was calculated as applied voltage divided by cathode-anode distance. Secondary electron emission yield ( $\delta$ ) was mapped by a scanning primary electron beam technique before and after field emission measurements. All measurements reported here are from samples without surface damage from micro-discharges.

## RESULTS AND DISCUSSION

Even if one assumes that the back contact barrier controls emission current, it is difficult to predict which particular factor dominates. There are at least 3 groups of factors: a) work function of metal, b) interfacial layers (metal oxides, carbides, oxy-carbides etc.), which can be modified by carbon film pre-growth treatments, and c) morphology of the metal surface.

Fig. 1 shows  $J(E)$  curves for carbon films deposited on n- and p-type Si and Sital coated by Ti ( $\phi = 3.95 \text{ V}$ ), Ni ( $\phi = 4.5 \text{ V}$ ), Cu ( $\phi = 4.4 \text{ V}$ ), or Pt ( $\phi = 5.32 \text{ V}$ ). Work function values,  $\phi$ , were taken from ref.[8]. The  $J(E)$  curves for the various samples vary due to the material of the back contact. In the case of Si substrates, emission from n-type arose at considerably lower field than from p-type. If we define the threshold field,  $E_{\text{th}}$ , as that field at which  $I = 10^{-8} \text{ A/cm}^2$ ,  $E_{\text{th}} = 1.5 \text{ V}/\mu\text{m}$  for n-Si substrates, but  $4 \text{ V}/\mu\text{m}$  for p-Si. This behavior can be understood if the back contact controls emission current: electrons moving from the contact to the carbon layer would «see» a lower and thinner tunneling barrier for n-Si. The films were highly resistive «in-plane» ( $10^{12} \text{ ohm-cm}$ ) but several orders of magnitude lower in the perpendicular direction, presumably due to vertical pores seen in SEM. They were sufficiently conducting to preclude charging effects during electron beam measurements. Their high resistivity should not influence  $E_{\text{th}}$  because of the low current at threshold. At high current, the film's resistivity may reduce emission although resistivity of the substrates remains negligible.

Milne et al.[5] studied ta-C films deposited on doped silicon but found no difference in threshold field for the samples on n- and p-Si substrates  $E_{\text{th}}^* \approx 8 \text{ V}/\mu\text{m}$ , where  $E_{\text{th}}^*$  is the field producing a current density  $J = 1 \mu\text{A/cm}^2$ . To further pursue the effect of substrate on the threshold field, we prepared silicon-carbon films from  $4.5\% \text{SiH}_4 + 2.5\% \text{C}_6\text{H}_{14} + 93\% \text{H}_2$  mixtures (other deposition parameters were the same as for the NDC films) on n- and p-Si substrates and on Sital coated by Ti. The silicon-carbon layer was deposited simultaneously on all the substrates.  $J(E)$  characteristics, as seen in Fig. 2, clearly show  $E_{\text{th}}(\text{Ti-contact}) < E_{\text{th}}(\text{n-Si contact}) < E_{\text{th}}(\text{p-Si contact})$ . Thus, the Fermi level position significantly influenced the field electron emission in the low field region for our carbon-silicon films as well as our NDC films. It should be noted that  $J(E)$  curves in the films studied could be rather well fitted by the power law  $J \propto E^\alpha$  where  $\alpha=2-4$  (Figs 1b, 2b) as previously observed [7]. Even lower  $E_{\text{th}}$  was observed

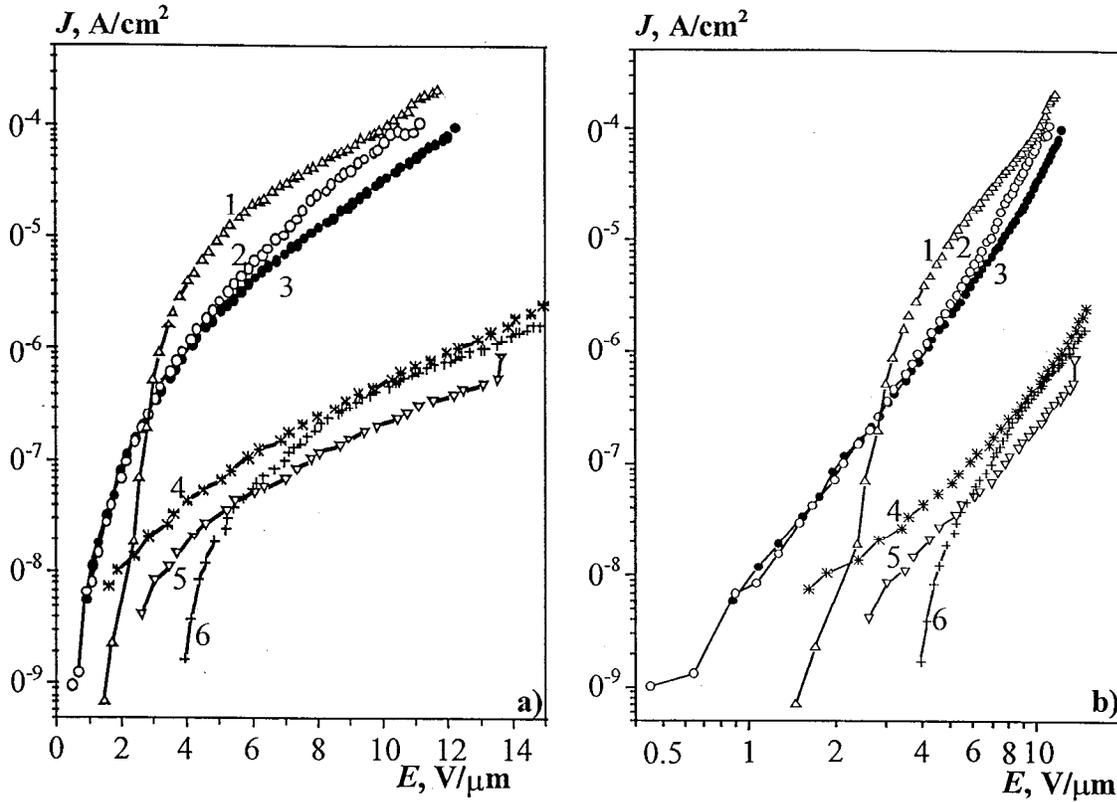


Fig. 1: Emission current density versus field in semilog (a) and log-log (b) scales for carbon film (process C214) on different substrates: 1:Ti; 2:Ni; 3:Pt; 4:n-Si; 5:Cu; 6: p-Si.

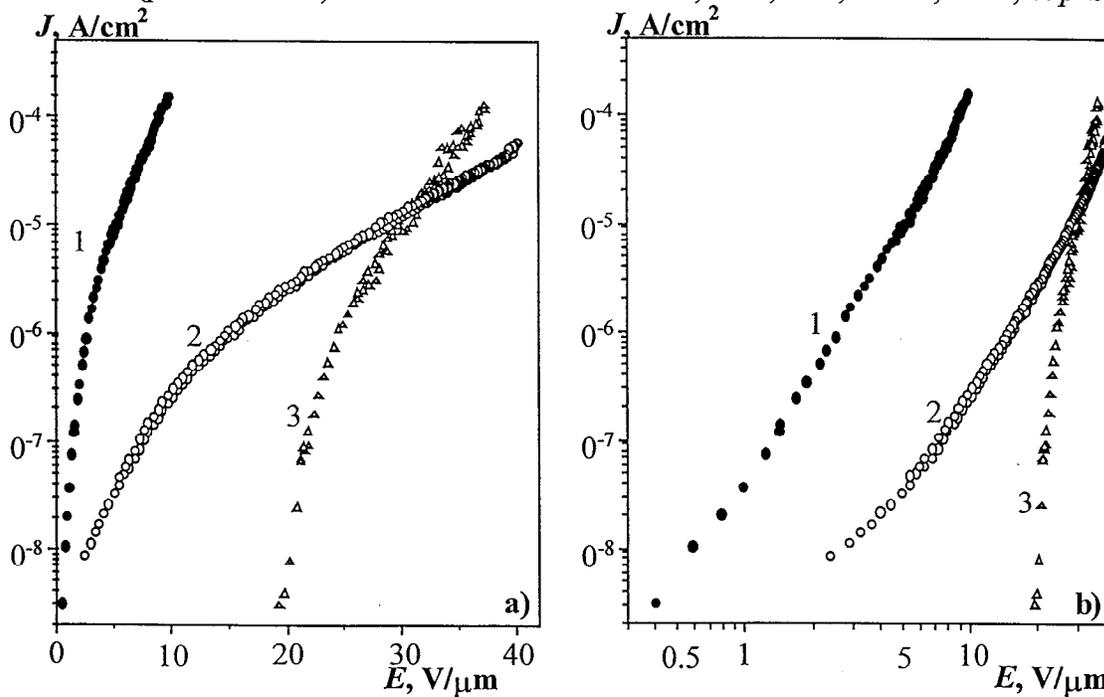


Fig. 2: Emission current density versus field in semilog (a) and log-log (b) scales for silicon-carbon layer (process SiC-209) on different substrates: 1) Ti on Sital, 2) n-Si and 3) p-Si

with some metals (Ti, Ni, Pt), figure 1. But the behavior of the samples with different metals was unexpectedly complicated. No direct correlation between work function and threshold field was observed (e.g. the sample with the Pt contact demonstrated a rather low threshold, practically the same as that with the Ni contact, despite their difference in work functions). AES and EELS showed that the carbon films had the same composition on the various substrates.

The lack of direct correlation between work function and threshold field, led us to study the microstructure of the metal films by scanning electron microscopy (SEM). Micrographs were taken for metal layers before and after carbon film deposition and varied from «grainless» Pt to large grained (about 200-500 nm) Cu. Copper diffused through the carbon film. Carbon layers deposited on the metal layers reproduced the underlying metal microstructure. Some examples of SEM photographs for carbon films on different metal layers are shown in Fig. 3. The microstructure varied widely for the various films despite similar metal deposition regimes and carbon coating of these metal layers in a single run. The differing grain size of these metal layers suggested different substrate surface morphology and this was born out by Atomic Force Microscopy (AFM).

To understand the effect of roughness, a special kind of sample was prepared: on Sital and

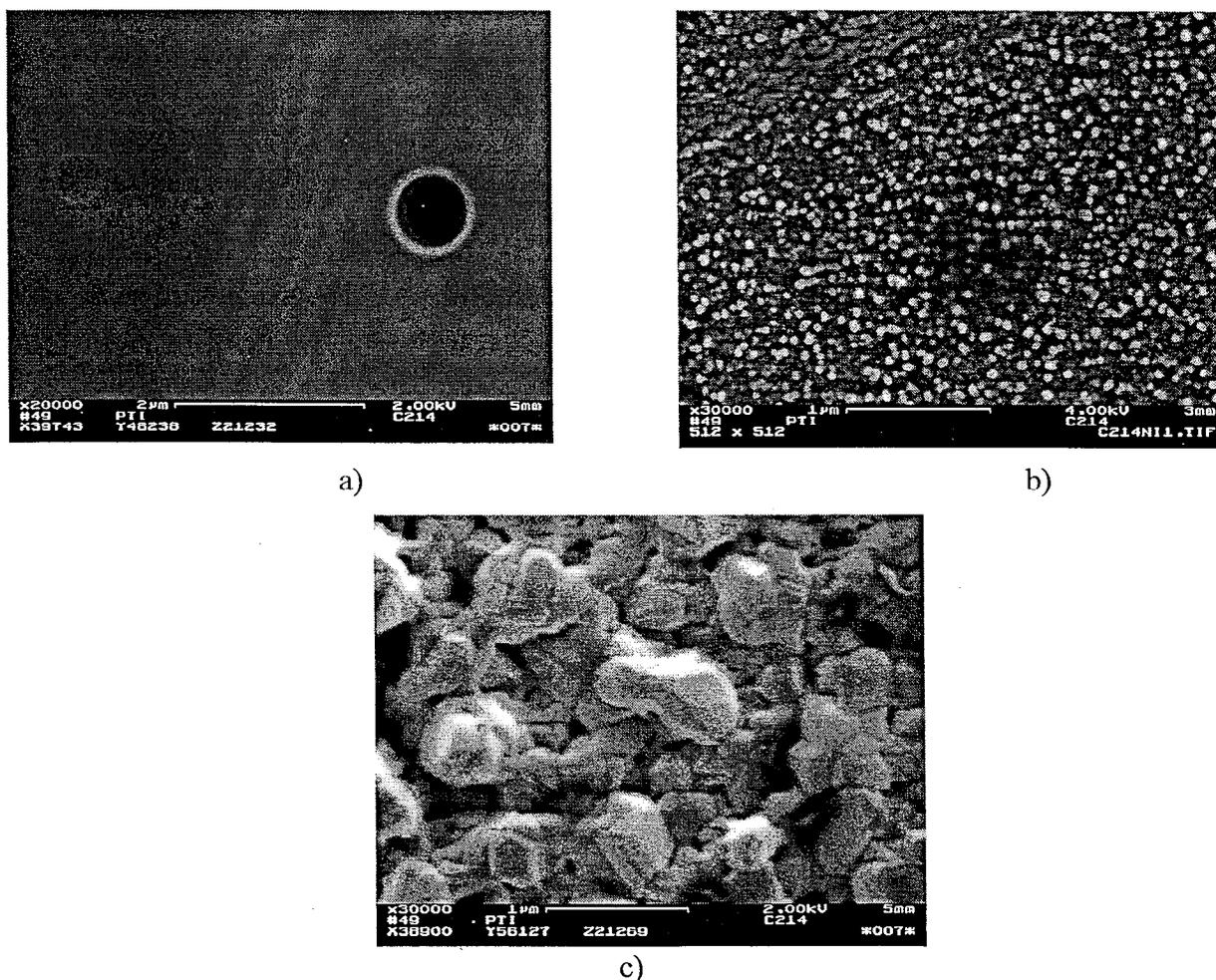


Fig.3 SEM micrographs of carbon layers on different metal deposited on Sital substrate as back contact: a) -Pt, b)- Ni, c) -Cu.

silicon substrates, copper films were deposited as before and were then coated by a thin Ti layer. It is known that such a Ti layer reproduces rather well the structure of the underlying morphology. Thus, we were able to fabricate back layers of Cu and Ti *with similar roughness*. Additionally, Ti does not diffuse well into carbon films. Samples with Ti layers deposited directly (i.e. without copper) onto different portions of the same substrates have been fabricated to be used as references. Field emission measurements from these samples are now ongoing and results will be reported later.

The mechanism of electron field emission from the samples studied must involve electron injection from the back contact into the carbon film, then transport of electrons through the carbon layer, and finally electron escape into the vacuum. We believe injection of electrons from the back contact is the "bottle neck" among this series of processes at least at low field.

## SUMMARY AND CONCLUSIONS

Electron field emission from hydrogen containing carbon films deposited by VHF CVD has been studied. The substrates were silicon and Sital coated by different metals. An effect of the back contact material on emission current vs field characteristics has been observed for these films as well as for silicon carbon films deposited by similar means. Lower threshold field was observed in the carbon films deposited on n-Si, Pt or Ni contacts than for p-Si. However, direct correlation to the work function of the back contact metal was not found presumably because of geometrical effects for the metals, as observed by SEM and AFM. These aspects of microstructure and surface morphology need more detailed study. We suggest that a proper model of electron field emission should predict a power law description in the low field region.

## ACKNOWLEDGEMENT

This work was funded by Sandia National Laboratories, grant SNSF 7IP51838. The work of TEF was performed under the auspices of the U.S. Department of Energy by Lawrence Livermore National Laboratory under contract No. W-7405-Eng-48. The authors wish to thank Dr. C. Neururer from Fribourg University, Switzerland for SEM characterization and A. Freudentahl of Sandia National Laboratories for contract administration.

## REFERENCES:

1. R.J.Nemanich, P.K.Bauman, M.C.Benjamin, S.W.King, J. van der Weide, R.F.Davis, *Diamond and Related Materials*, **5**, 790 (1996).
2. M.W.Geiss, J.T.Twichell and T.M.Lyszczarz, *J.Vac.Sci.Tech.*, **B14**, 2060, (1996).
3. J.Robertson, *Mat.Res.Symp.Proc.*, **471**, 217, (1997).
4. A.P.Burden, R.Forest, S.R.P.Silva, B.J.Sealy and G.A.J.Amaratunga, *Mat.Res.Symp.Proc.*, **498**, 221 (1998).
5. W.I.Milne, J.Robertson, B.S.Satyanarayana, A.Hart and B. Kleinsorge, *Mat.Res.Symp.Proc.*, **498**, 209, (1998).
6. A.I.Kosarev, V.V.Zhirnov, A.J.Vinogradov, M.V.Shutov, L.V.Bormatova, E.I.Givargizov, and T.E.Felter, *MRS Symp.Proc.*, **509**, 139 (1998).
7. A.I.Kosarev, A.N.Andronov, S.V.Robozerov, T.E.Felter, A.J.Vinogradov, V.V.Zhirnov and M.V.Shutov, *IVMC-98, Abstracts*, p.265.
8. *Handbook on Electrotechnical Materials*. Ed. By J.V.Kornitskij et al., Leningrad, 1988.

