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ELECTRON FIELD EMISSION FROM UNDOPED AND DOPED DLC FILMS

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ABSTRACT

In this presentation the electron field emission and electrical conductivity of ~~the~~ undoped and nitrogen doped DLC films have been investigated.

Undoped and nitrogen doped DLC films were grown by PE CVD ~~method~~ from $CH_4:H_2$ and $CH_4:H_2:N_2$ gas mixtures, correspondingly. During nitrogen doped DLC film~~s~~ deposition, the nitrogen content in the gas mixture was varied within the range ~~from~~ 0 to 45%. In-situ ~~the~~ gas-phase doping allowed us to deposit DLC films with different content ~~of~~ nitrogen ~~in them~~. DLC films were deposited under three different levels of gas pressure in the chamber: 0.2, 0.6 and 0.8 Torr.

The measurements of emission current from samples were performed in the vacuum system which could be pumped to a stable pressure of 10^{-6} Torr. The emission current was measured in the diode structure. The emitter-anode spacing L was constant and equal to 20 μm.

The current - voltage characteristics of the Si field electron emission arrays covered with undoped and nitrogen doped DLC films show that at the beginning the threshold voltage (V_{th}) remarkably increases with nitrogen content ~~growth~~, then ~~the decreasing of~~ V_{th} is observed to decre and finally V_{th} increases. Corresponding Fowler-Nordheim (F-N) plots follow F-N tunneling over a wide ~~field~~ range. The F-N plots were used for determination of the work functions, threshold voltage, field enhancement factors, and effective emission areas.

For the qualitative explanation of experimental results, we ~~base on the model of~~ treat the DLC film as a diamond-like (sp^3 - bonds) matrix with graphite-like inclusions in it.

INTRODUCTION

DLC films are very attractive for field emitter applications. Previous results on DLC coating demonstrated very substantial enhancement of field emission due to the coating of the silicon tips with DLC films [1-5], but the influence of the preparation conditions of DLC films on their properties still has to be investigated. The doping with nitrogen strongly influences the emission properties of DLC films [6-8]. Nitrogen is ~~a~~ very suitable ~~atom~~ as a n-type dopant because the atomic size is similar to C and it is a donor in diamond and DLC film.

In spite of the intensive investigations, the influence of the DLC film deposition conditions and nitrogen doping on DLC film properties is not well understood.

In this work, the electron field emission properties of silicon tip arrays coated with undoped and nitrogen doped DLC films are investigated. The properties of the DLC films strongly depend on the microstructure which can be varied by the deposition conditions. The influence of the DLC films deposition conditions on field electron emission is studied in detail. The correlation between the film properties and field emission characteristics is investigated.

EXPERIMENT

Cathode formation

The arrays of silicon emitters tips were fabricated by forming the silicon points by wet chemical etching. The cathodes are formed on (100) Si n-type wafers ($N_d=10^{15}$ cm^{-3}) by patterning with Si_3N_4 as masking material. The tip sharpening was performed by oxidation of the as-etched tips at 900^{0}C in wet oxygen. After the oxidation, the oxide is removed in $HF:H_2O$ solution. This sharpening technique allows the production of tips with a radius of curvature of 10-20 nm. The height of the silicon tips was 4µm. The arrays have been fabricated over areas of 8x8 cm^2. The tip density was 2.5x10^5 tips/cm^2. The radii before and after DLC films deposition were estimated by scanning electron microscopy.

DLC films with different thicknesses in the range of 60-80nm were grown on ~~the~~ flat silicon wafers and on silicon tip arrays by plasma enhanced chemical vapor deposition (PE CVD) ~~method~~ from a $CH_4:H_2:N_2$ mixture. Nitrogen content in the gas mixture was varied within the range ~~from~~ 0 to controll- 45%. In-situ-gas-phase doping allowed ~~to deposit~~ DLC films deposition with ~~a different content of~~ nitrogen content ~~in them~~. DLC films were deposited under three different levels of gas pressure in the chamber: 0.2, 0.6 and 0.8 Torr. The substrates for deposition of DLC films were put directly on the cathode of diameter 200 mm which was cooled by water and capacitively connected to a 13.36 MHz generator. During the plasma decomposition experiments, RF bias voltage was about 1900 Volts. The DLC coatings were smooth enough and have reproducible properties from sample to sample under the same deposition conditions.

Measurements

The measurements of the emission current were performed in a vacuum system which could be pumped to ~~the~~ a stable pressure of 10^{-6} Torr. The emission current was measured in the ungated cathode-anode diode structure.

The emitter-anode spacing L was constant and equal to 20 µm. We fabricated a test diode ~~construction~~ by "sandwiching" ~~of~~ anode and cathode plates. A silicon wafer was used as the cathode and a molybdenum wire or quartz plate coated with ITO (indium-tin oxide~~s~~) was used as an anode. A 20 micron high fluorplast film spacer was used to keep the two plates separated from each other. The emission current-voltage characteristics were obtained with a current sensitivity of 5 nA over a voltage range up to 1500 V. A 0.56 MΩ resistor was placed in series with the cathode to provide short-circuit protection.

After ~~T~~the tip array (8×8cm^2) was completely fabricated, ~~formed and the~~ 1 cm^2 squares were cut from the wafer and mounted into the vacuum station. The control silicon emitter tip array (without coating) was dipped in a 5% HF solution for 20 s to remove the native oxide layer immediately before mounting in the HV system. The investigated cathode area for ~~one~~ each measurement was 5.5×10^{-3} cm^2 and it contained 1.4×10^3 tips.

The resistivity of DLC films was determined from I-V curves of MIS structures at an electric field strength 10^6 V/cm. The thickness and refractive index of the DLC films on flat silicon wafers was measured with ~~the~~ laser ellipsometry (λ=632.8 nm). To estimate the nitrogen content in DLC films, the Auger method was used.

RESULTS AND DISCUSSION

The flow of N_2 in the gas mixture $SiH_4:H_2:N_2$ ~~under~~ during DLC film deposition was varied to control the N content in the DLC film. Increasing ~~of~~ the N_2 flow ~~content results in~~ increas~~ing~~es ~~of~~ the N content in the DLC films ~~and it depends on gas mixture pressure~~ (Fig.1).

The current - voltage characteristics of the Si field electron emission arrays covered with undoped and nitrogen doped DLC films are presented in Fig. 2a. At the beginning, the threshold voltage (V_{th}) remarkably increases with nitrogen content ~~growth~~, then ~~the~~ decreasing of V_{th} is observed and finally V_{th} increases. Corresponding Fowler-Nordheim (F-N) plots are shown in Fig. 2b. The curves follow~~s~~ F-N tunneling over a wide field range. The F-N plots were used for determination of the threshold (turn-on) voltage, work function~~s~~, field enhancement coefficients, and effective emission area~~s~~ according to the procedure described in Refs.9-12. It is impossible to independently determine two parameters: the field enhancement coefficient (β) and work function (Φ) from the Fowler-Nordheim plot alone. The field enhancement coefficients were calculated from the geometry of the emitting system according to

$$\beta = (h/(r+d)) / L \qquad (1)$$

where r is the radius of the tip estimated with SEM, h is the height of the tip, d is the thickness of DLC film, and L is the emitter-anode spacing. For the case of silicon tips without DLC ~~covers~~ coating, the field enhancement coefficient was determined from the Fowler-Nordheim plot for silicon (Φ=4.15 eV). The good agreement between β calculated from equation (1) for case d=0 and determined from Fowler-Nordheim plot is observed.

The effective work function for different DLC film coatings were determined from the slope of Fowler-Nordheim plots (b) using the calculated β coefficient. The relation of the work functions of two materials (silicon and silicon covered with DLC films) was used.

$$\Phi_1/\Phi_2 = (b_1\beta_1/ b_2\beta_2)^{2/3} \qquad (2)$$

where Φ_i, β_i and b_i are the work functions, field enhancement coefficients and curve slopes in the Fowler-Nordheim equation, respectively, and index i=1 for uncoated silicon tips and i=2 for ~~the~~ ones coated ~~covered~~ with DLC film.

dependence of the

The dependence~~s~~ of threshold voltage and ~~the~~ effective work function on the N_2 in the gas mixture is ~~are~~ presented in Figs. 3, 4. For comparison, the threshold voltage and effective work function of Si tips without DLC coatings are shown. Nonmonoton~~ous~~ic dependences on N content are measured. An increase ~~growth~~ of effective work function is observed in the initial part of the curve. A further increase of N content causes the decrease of Φ. At high N_2 concentration, the growth of Φ is observed again. The lowest value of Φ=0.92 eV was obtained for DLC films deposited at N_2=25% in the gas mixture. A significant influence of the gas pressure on effective work function is also observed. As can be seen from Figs.4a,b, ~~the~~ a correlation exists in V_{th} and Φ dependencies. This points out that emission efficiency is caused not only by the effective work function but by the DLC film's conductivity ~~also~~. as well.

The, resistivity of the DLC film on N_2 content in the gas mixture ~~dependence~~ was also measured. The ~~increase of the~~ resistivity with N_2 content ~~growth~~ increases at the beginning with the and then f~~ollowing~~ decreas~~ing~~es ~~is observed~~.

An optical band gap of the DLC films has been measured by using spectroscopic ellipsometry. The band gap is changed significantly with N content in the DLC film. In the case of nitrogen doped DLC film, the smallest value of E_g is observed (Fig.5).

Values of the band gap reach up to 4eV at higher N_2 content. Our experimental results concerning the influence of the nitrogen doping on DLC film properties are in agreement with data obtained by other authors [6,7,9].

Nitrogen atoms in DLC films stabilize carbon atoms in sp^3 sites with the C-N bonds creation. of At the same time, nitrogen is the donor-type impurity in diamond and DLC films. Undoped DLC film shows p-type conductivity. Under low levels of nitrogen doping in DLC, the n-type donor impurity compensates the p-type. As a result, the conductivity of DLC film is decreased. When the N content is less than 1.7 at % the emission current is less than that of undoped DLC film, probably due to the higher resistance of compensated DLC film.

The continuous shift of Fermi level towards the conduction band occurs with ~~growth of~~ increasing N content in the film. This causes an increase in the emission current and a decrease of threshold voltage (see Fig.3). The effective work function decreases, but further growth of N content promotes the band gap increase (see Fig.4,5) due to the sp^3 bond growth and, consequently, the effective work function is increased. As a result, the dependence of the effective work function on N content has a minimum. According to the model of the DLC film~~s~~ as a diamond-like matrix with graphite-like inclusions in it, these films are not a homogeneous material and have the thickness and spatial heterogeneity of their structure which is caused ~~with~~ by the deposition conditions. To characterize such films, we used the "effective" work function.

The nonmonoton~~eous~~ic dependencies of E_g (Fig.5) on nitrogen content in the gas mixture may be interpreted in the framework of a model taking into account the effect of nitrogen on the film structure. At low concentration, the nitrogen atoms fit into the film at sp^2-clusters boundaries increasing the fraction of the disordered sp^2-phase[10,11]. This, in turn, must result in E_g decreasing, which is actually observed (See Fig 5). On further increasing the nitrogen content in the film, the excess nitrogen atoms begin to fit in between the sp^2-clusters. This causes strain relaxation in the film and stimulates formation of sp^3-coordinated carbon-hydrogen bonds. As this takes place, E_g increases.

The relationship among work function, electron emission and conductivity should be studied further to clarify the emission mechanism of DLC films.

CONCLUSION

We have studied the electron field emission from silicon tip arrays coated with undoped and nitrogen doped DLC films. The doping level was changed by varying the nitrogen content in gas mixture $CH_4:H_2:N_2$ Nonmonoton~~eous~~ic dependences of effective work function, threshold voltage, resistivity and optical band gap on nitrogen content in DLC film are observed. The minimum effective work function was in case of $N_2=25\%$ in the gas mixture, and found to be 0.92 eV. We proposed an explanation of the experimental results on electron field emission taking into account the work function, band gap and conductivity. Using a silicon tip array covered with undoped and in-situ nitrogen doped DLC films leads to an increase of electron emission currents in comparison with uncoated arrays.

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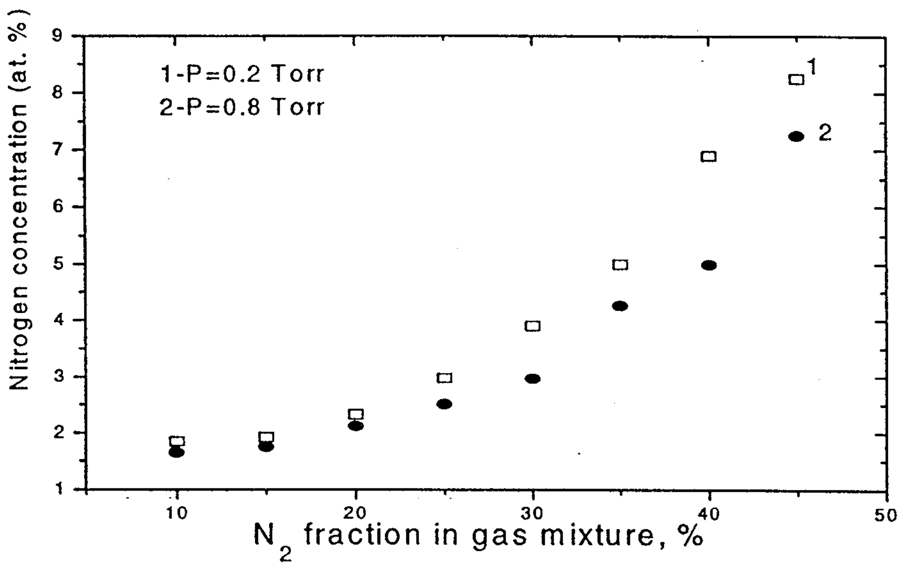

Fig.1. Nitrogen concentration in DLC film on nitrogen fraction in gas mixture dependences; 1-P=0.2Torr; 2-P=0.8Torr.

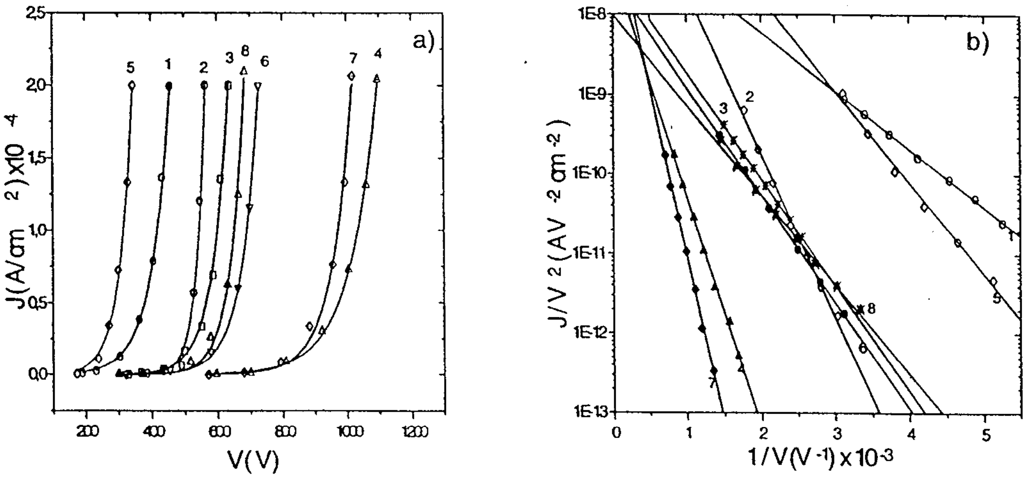

Fig.2. Current - voltage characteristics and corresponding Fowler-Nordheim plots of the Si tip arrays coated with undoped and gas phase doped DLC films: (1-8) Si tip arrays +DLC: 1 - $C(N_2)$ - 0% 2 - 5%; 3 - 10%; 4 - 15%; 5 - 20%; 6 - 25%; 7 - 30%; 8 - 35% (P=0.8 Torr, $C(N_2)$ - nitrogen content in gas mixture under PE CVD deposition).

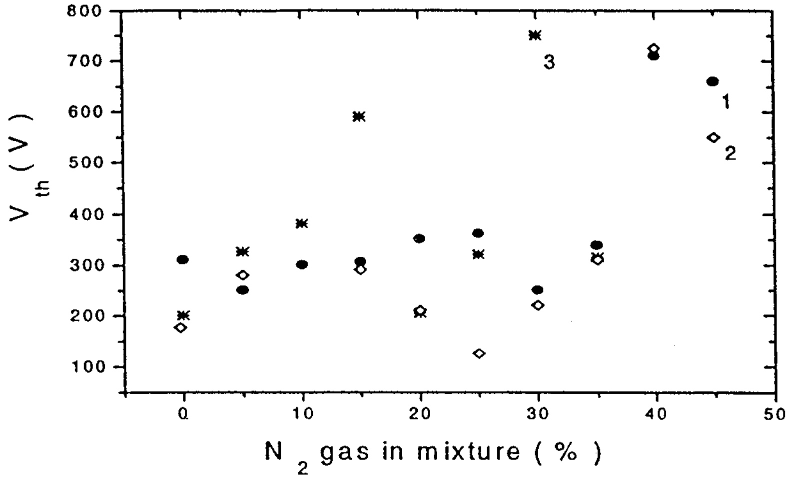

Fig 3. Threshold voltage under electron field emission from silicon tips+DLC films on nitrogen content in gas mixture dependences (1 - P=.0.2 Torr, 2 - P= 0.6 Torr, 3 - P=0.8 Torr)

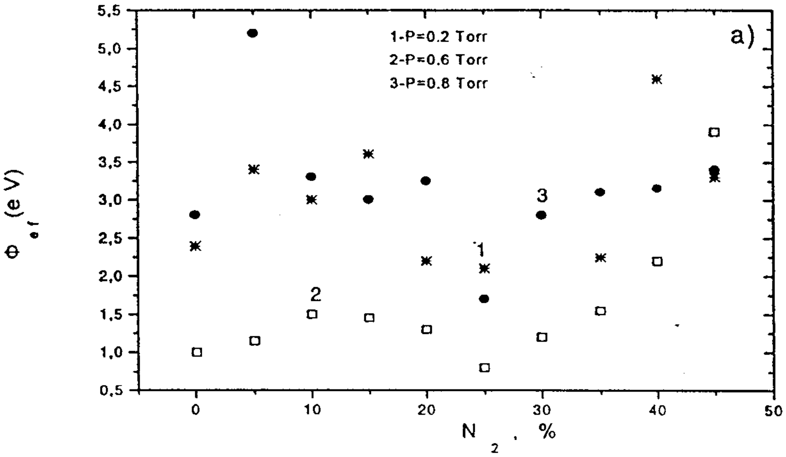

Fig 4 Effective work function under electron field emission from silicon tips+DLC films on nitrogen content in gas mixture dependences (1 - P=.0.2 Torr, 2 - P= 0.6 Torr, 3 - P=0.8 Torr)

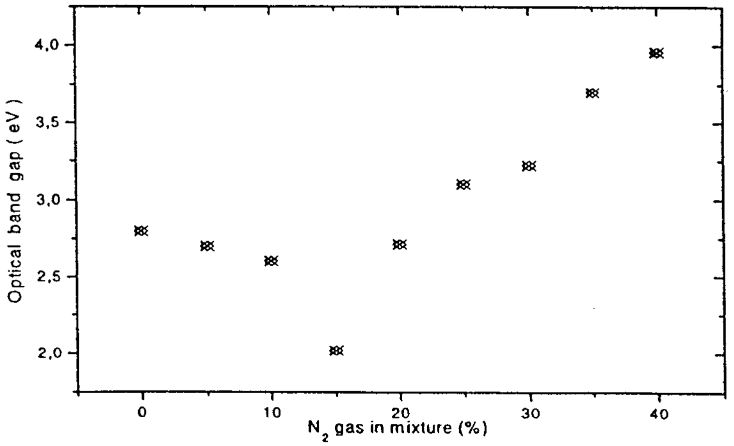

Fig.5. Optical band gap of DLC films on nitrogen content in gas mixture dependence (p=0.8 Torr)