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Decrease of electron paramagnetic defect density and enhancement of electron field emission in annealed carbon films

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We have studied the effect of the paramagnetic defects in carbon films on the field-emission properties. The paramagnetic defects in carbon films originating from the carbon dangling bonds were measured using electron spin resonance (ESR). We found a reduction of the dangling bond density in the annealed carbon films in N_2/H_2 atmosphere from ESR spectroscopy. The annealed films with lower defect densities, i.e., dangling bonds, showed an improved characteristic of higher emission current density as well as a lower turn-on electric field in the Fowler–Nordheim type tunneling. Also in the annealed carbon films a correlation is observed between the decrease of band gap estimated from the electrical conductivity and the reduction of dangling bond density. The earlier results indicate that the enhancement of the emission current level in the annealed carbon films is related to the decrease of the ESR centers. [S0021-8979(00)05310-X]

I. INTRODUCTION

The potentials of the electron field emission as a flat panel display technology have been well known in the literature and lots of efforts have been spent in examining the emission properties of the plane cold cathodes made of thin carbon-based films.[1–4] Amorphous carbon *a*-C, hydrogenated *a*-C:H, and nitrogenated *a*-C:H:N films with their large area deposition capabilities at low temperature and the low threshold voltages for electron emission have been attracting a great deal of interest in the field-emitter applications as well as from the basic physical point of view. Changes in the electronic properties by various treatments such as ion implantation, plasma bombardment, and annealing are generally accompanied with a deformation of the electronic structure in the materials, which results in defect levels in the gap region.[5,6] Also it leads to a creation of different kinds of trapping centers in the band tail regions. In general, there are two forms of amorphous carbon, the black semiconducting films called as DLC (or tetrahedral amorphous carbon) and the hydrogenated *a*-C:H (or nitrogenated *a*-C:H:N). Recently, the electron spin resonance (ESR) technique has been used to study the correlation between the defect densities and the field electron emission properties in the hydrogenated diamond films.[7,8] The results indicated that diamond films with high defect densities, i.e., spin density, show an improved characteristic of high emission current density and a low threshold electric field. Furthermore, the reports suggested that the observed defect centers, i.e., ESR centers, originate from the carbon dangling bonds in the nondiamond as well as in the diamond region.

In this work, first, the enhancement of electron emission properties in the annealed carbon films is reported and discussed, which are formed by conventional rf magnetron sputtering from a graphite target in Ar atmosphere. The main interest of this article is to study the nature of the defect centers in carbon films and their relation to the electron emission characteristics. ESR Raman spectroscopy, and atomic force microscopy (AFM) were employed for the analysis.

II. EXPERIMENT

Carbon (*a*-C) films of 50 nm thick were deposited at room temperature by conventional rf magnetron sputtering from a carbon target (purity 99.999%; 4 in. diameter) in Ar atmosphere on Cr (200 nm)/SiO_2 (1000 nm)/*p*-type Si (111) wafer ($\rho \sim 10–20\ \Omega\,\mathrm{cm}$). Ar flow rate was set as 8 sccm and the pressure was kept at 5 mTorr to optimize the adhesion quality of carbon, and rf power was fixed at 200 W. In order to study the effect of the nitrogen (or argon) and hydrogen on the quality of the carbon films, we annealed at 400 °C in either N_2/H_2 or Ar/H_2 mixture for some selected parts of the specimens. The annealing temperature was determined by considering the softening temperature of the sodalime glass substrates typically used for field emission displays. The electron field emission characteristics of the films were measured using a diode geometry in the ambient light. The changes of the defect properties were investigated using ESR spectroscopy at 300 K in the dark and under ambient light. Raman spectroscopy was performed on the same samples

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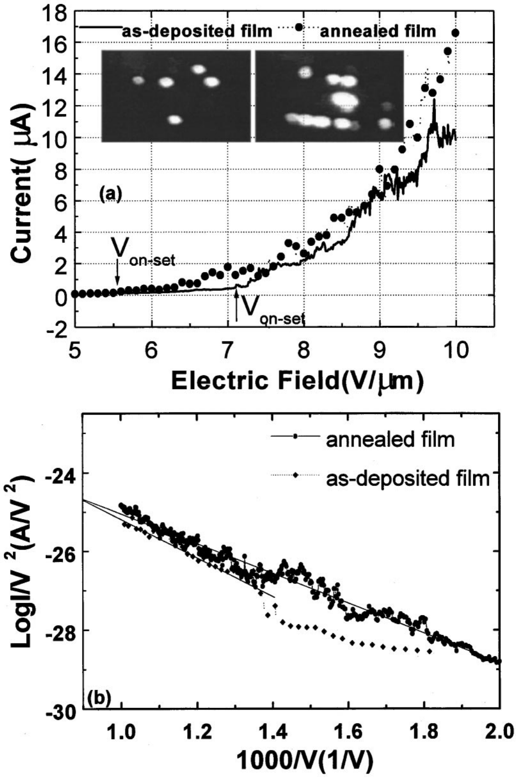

FIG. 1. (a) Emission current–electric field characteristics and (b) F–N plots for the films with and without annealing, respectively. Inset shows emission site density captured by charge coupled device camera for as-deposited (left) and annealed carbon film (right). Vertical scale is about 5 mm.

before and after annealing at 400 °C. The spectra were excited by 1064 nm Nd–yttrium–aluminum–garnet laser with a power of 100 mW.

The electron emission measurement was performed on the carbon films in the ambient light, which is a normal operating condition for the flat panel display. An anode [indium tin oxide (ITO) glass] was placed directly above the carbon film using a 100-μm-thick spacer and was applied with a high voltage. Field emission testing was performed in a vacuum better than 10^{-7} Torr using the Keithley 237 source-measure unit. The samples were subjected to an increasing bias until a maximum voltage of 1100 V was reached. If any emission was observed, the activation voltage was turned back to zero and the same cycle was repeated several times to verify the results. To estimate the spatial distribution of emission centers over the sample surface, a yellow-orange light emitting ZnS:Mn thin film phosphor coated on ITO/sodalime glass was used as the anode plate.

III. RESULTS AND DISCUSSION

Figure 1 shows typical emission current (I)–applied electric field (E) characteristics. The inset of Fig. 1(a), typical images of the emission sites projected from ITO glass for all types of carbon films, indicates that the density of emission sites for the as-deposited a-C films is concentrated near the edges of films. A general improvement after the annealing treatment is observed as the emission area expands to the whole film. Furthermore the improvement of the emission site density appears to be independent of the types of annealing employed in this work. The emission current (I)–applied electric field (E) characteristics are shown in Fig. 1(a). A considerable hysteresis in the first measurement of the as-deposited carbon film is greatly reduced for the annealed carbon film. In general, this hysteretic effect indicates the presence of an on-going structural change that may be accompanied with the microscopic changes in the film morphology. For the annealed films we observed a lower on-set electric field of about 5.5 V/μm compared to about 7.4 v/μm for the as-deposited films. The saturation current density is also improved by approximately a factor of 2 compared to that of the as-deposited films. In Fig. 1(b) we can also see the decrease of the effective work function near the turn-on region after annealing, that was deduced from the decrease of the slopes in the Fowler–Nordheim (F–N) plot.

Raman spectroscopy was performed on the same samples before and after annealing at 400 °C. The Raman spectra of all the films, as shown in Fig. 2, decomposed into three peaks located at 1290, 1470, and 1580 cm^{-1}. The peak at 1470 cm^{-1} observed for all films is attributed to the nanocrystalline diamond phase,[9–11] and this peak is decreased after annealing in either N_2/H_2 or Ar/H_2. A nanocrystalline phase has been observed in amorphous-graphite nitrogen-free films. A peak near 1580 cm^{-1} (G band) is found in the amorphous film, which is assigned to C–C stretch mode with a contribution from the different bond lengths and angles in the sp^2-bonded carbons. The shift of the D-band resonance peak from 1332 to 1290 cm^{-1}, the characteristic sp^3-bonded carbon Raman peak, varies with the size of crystallites and the strain.[12] In general, the D band becomes active when small crystallites are present. Taking into account the 50 times greater efficiency of Raman scattering of the graphitic sp^2 compared to that of the crystalline diamond,[13] the ratio of the line intensities is evidence of insignificant amount of sp^2-bonded carbons in our films. However, after annealing, a large amount of the sp^2-bonded carbons was confirmed within the whole matrix regardless of the annealing atmosphere.

The morphological images studied by the AFM are shown in Fig. 3. The smooth surfaces before annealing with an average roughness of 18–24 nm, depending on the area scanned, was transformed into the surfaces with a rms roughness of 31–38 nm after annealing. The increase of the surface roughness is more pronounced in films annealed in N_2 gas especially. The surface roughness depends on the degree of crystallinity in the carbon film, as such for films containing finer-grained crystallites and larger fraction of the amorphous phase,[14] the average roughness will be lower. This readily explains the observed rapid reduction of the ESR signal for the annealed sample as shown later, since the annealing promotes the growth of larger crystallites, consequently increases the roughness of films and reduces the number of defect centers that are the sources of the ESR signal.

Typical ESR signals for the as-deposited and the annealed carbon films are shown in Fig. 4. A large signal corresponding to the unpaired single electrons at $g = 2.004$ is immediately apparent in the case of as-deposited film. Upon

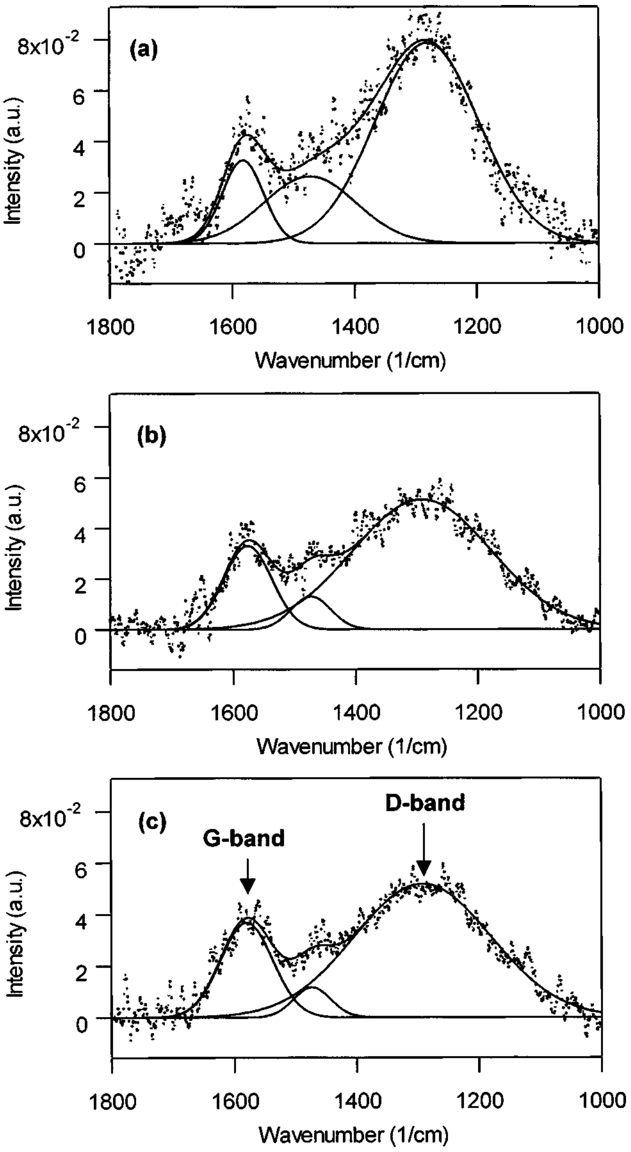

FIG. 2. Deconvoluted Raman spectra of amorphous carbon films show a large reduction of the intensity of the peak 1300 cm^{-1} after the annealing. The characteristics bands, denoted as *G* for the Raman allowed graphite mode and *D* for the disorder-induced mode near 1300 cm^{-1} are observed in the first order Raman spectra.

annealing in N_2/H_2 atmosphere, this peak disappears. Based on the result reported in Ref. 15, we can estimate a few orders of magnitude reduction in the spin density between the nonhydrogenated amorphous and the hydrogenated carbon films although we cannot determine the absolute concentration. Therefore, one possible reason for the absence of the ESR signal in the annealed films in N_2/H_2 atmosphere could be due to the fact that either the hydrogen partially saturates the dangling bonds or the film may release internal stress responsible for the unpaired spins by decreasing the coordination number.[15] Until now, it has been reported that increase of the defect centers results in the enhancement of electron emission level.[7,8] However, from the ESR and the conductivity measurement we observed a correlation between the increase of electrical conductivity, i.e., enhancement of the emission, and the reduction of spin density after

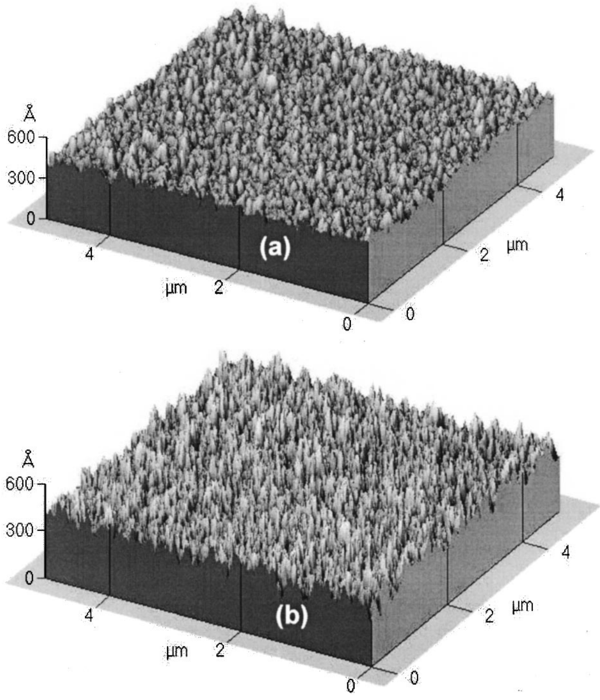

FIG. 3. The typical view of the surface on 50-nm-thick as-deposited carbon films (a); annealed films in N_2/H_2 mixed atmosphere (b) observed by AFM. The scanned area is 5×5 μm^2.

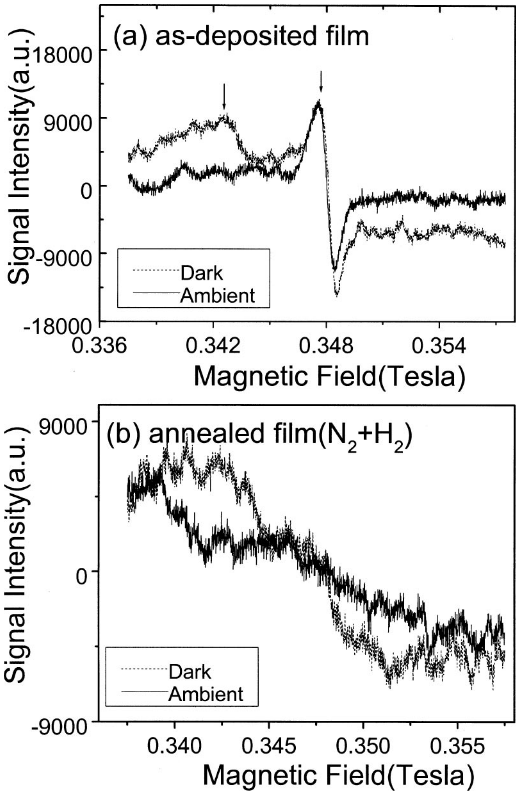

FIG. 4. The typical ESR signal observed for the as-deposited carbon films (a) and annealed film (b). The signal originated from a carbon dangling bond in the nondiamond phase carbon region.

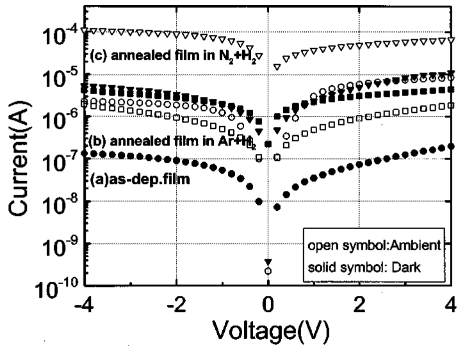

FIG. 5. $I-V$ curves for the as-deposited film and the annealed films in dark and under ambient light condition. The current levels are very sensitive to the light.

annealing in N_2/H_2 atmosphere. This indicates that annealing in N_2 atmosphere modifies the electronic structure of the material by reducing the defect density although the influence of H_2 cannot be neglected within the limited range. If we assume that the spins in the films come from sp^3 defects with a g value of about 2.004, upon graphitization by nitrogen these defects are healed by the forming sp^2 dominant phase, thus the spin density from sp^3 phase decreases. The annealing in N_2 atmosphere displaces the Fermi level towards the conduction band accompanied with an increase in the conductivity[16] and so, the donor electrons fall from the donor levels into the singly occupied defect levels, which become fully occupied and are no longer paramagnetic. As a result, the ESR signal disappears. However, we cannot rule out the possibility that the number of defects in the annealed films would be too small to be detected by the conventional ESR method.

The electronic states in a typical amorphous material such as *a*-Si:H consist of extended states, tail states, and deep states, originating from the long rage correlation the asymmetry, and the structural disorder, respectively. While information about the deep states can be easily obtained from the ESR spectra, the information about defects in the thin surface layer, i.e., the states lying near the band edges, is more difficult to obtain. In any case, it should be noted that the isotropic ESR signal corresponding to the disordered dangling bonds was not found in the annealed films throughout the measurement.

To get the information on the states lying near the band edges, the $I-V$ characteristics were measured. The $I-V$ curves of the carbon films at 77 K and ambient temperature measured by a two-probe method in the dark and under the ambient light are shown in Fig 5. For the as-deposited films, the current increased by about three orders of magnitude when it was exposed to the ambient light showing a large sensitivity to the light regardless of the direction of the bias. The difference between the reverse dark and the ambient currents for the annealed films in N_2/H_2 atmosphere was increased by about one order of magnitude, while no change was observed for the annealed films in Ar/H_2 with respect to the current levels, bias directions, and light exposures. On the other hand, in a separate experiment, the dependence of the conductivity of the as-deposited films on temperature in the low temperature range of 20–100 K showed insulator-like behavior indicating that a gap is created, whereas a finite conductivity is observed in the annealed films in the same temperature range indicating that a gap may not be present.

The enhancement of the electron emission level in the annealed films in N_2/H_2 atmosphere can be explained as follows. It is accepted that *a*-C film and hydrogen containing *a*-C are characterized by the presence of shallow localized states (SLS) appearing in the band edge region due to the sp^2 bonds and the deep states or dangling bonds appearing near the Fermi level.[17,18] When an amorphous material such as *a*-Si:H is illuminated with photons of energy nearly equal to the band gap, the carrier transport takes place by several discrete processes.[19,20] So, we may apply the same concept to the case of annealed carbon films. The photogenerated carriers in the ambient light are quickly trapped into the SLS near the band edges and they would contribute to the photoconductivity by thermal emitted into the extended states. From the fact that the F–N plot shows a single slope and combining this with the earlier concept, the electrons seems to be easily emitted outright from the surface under the electric field. On the other hand, for the as-deposited film, a different mechanism can be imagined. Photogenerated carriers may recombine or quench to form the charged defect states,[21] which appear as decreased spin density in the ESR signal in the ambient light. It can happen through a sequential trapping of those carriers to the deep level states distributed over some depth range, as confirmed from the multiple slopes in the F–N plots.

IV. CONCLUSIONS

In this work, the enhancement of the electron emission in the annealed nonhydrogenated carbon films was reported. The main interest of this article was to study the nature of the defect centers in the carbon films and their relation to electron emission characteristics. The ESR technique, Raman spectroscopy, and AFM were employed for the analysis. The annealing in N_2 atmosphere displaces the Fermi level towards the conduction band accompanied with an increase in the conductivity. The absence of the ESR signal in the annealed film in N_2/H_2 suggests that the hydrogen saturates the dangling bonds or releases the internal stress responsible for the unpaired spins by decreasing the coordination number. The formation of more homogeneous composition confirmed from the larger emission area is one of the advantageous effects of the annealing in N_2/H_2 mixed atmosphere.

It should be noted that the rf sputter-deposited *a*-C films using Ar gas may show a different behavior compared to the chemical-vapor-deposited (CVD) films since the sputtering process is intrinsically statistical in character. The deposition species are mainly C neutrals but a few C^+ ions and energetic Ar species (neutrals and/or ions) are present during the deposition. Since Ar species are bigger and heavier than C^+ ions, larger momentum of Ar species could result in a different morphology compared to the CVD films, thus giving rise to a modified conduction and/or emission mechanism. Therefore, more systematic and comparative studies with the CVD films are needed for a better understanding of the annealing effect in sputtered films.

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