

# Effects and thermal stability of hydrogen microwave plasma treatment on tetrahedral amorphous carbon films by *in situ* ultraviolet photoelectron spectroscopy

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This paper reports a comprehensive experimental study on the effects of hydrogen microwave plasma treatment on nonhydrogenated high  $sp^3$  content tetrahedral amorphous carbon (ta-C) film. In this study, a surface C–H dipole layer was first observed by high resolution electron energy loss spectroscopy, showing the presence of C–H bonding states. This resulted in the enhancement of electron field emission of the plasma treated films by largely lowering the turn-on field. Thermal stability tests using *in situ* ultraviolet photoelectron spectroscopy confirm that the C–H dipole layer not only reduces the work function of the films, it is extremely stable in both ambient and vacuum conditions and can sustain up to 600 °C annealing in vacuum. Atomic force microscopy studies also show minimal modifications to the surface morphology, leading to the conclusion that the C–H dipole layer is responsible for lowering the work function. This has improved the electron emission properties which can lead to potential applications such as electron emission displays. © 2009 American Institute of Physics. [DOI: 10.1063/1.3156689]

## I. INTRODUCTION

It is a well known fact that hydrogen-terminated surface of crystalline diamond exhibits many interesting properties that differs from the bulk properties.<sup>1</sup> Hydrogenated diamond surfaces are known to have high surface conductivity and negative electron affinity with extraordinary field emission properties. This is mainly due to the presence of a surface C–H dipole layer which lowers its work function.<sup>1</sup> A similar material to that of crystalline diamond but having an amorphous phase is diamondlike carbon. There are two different types of diamondlike carbon films, hydrogenated and nonhydrogenated films. The type of film depends on the deposition techniques used for the growth process.<sup>2</sup> Usually, gas-phase deposition techniques such as plasma enhanced chemical vapor deposition will induce the growth of the hydrogenated diamondlike carbon films, while high-vacuum ion-beam deposition techniques such as the pulsed laser deposition (PLD) technique or filtered cathodic vacuum arc (FCVA) technique will induce growth of hydrogen-free diamondlike carbon films. Hydrogenated diamondlike carbon films tend to have low Young's modulus, low hardness, and low  $sp^3$  content.<sup>2,3</sup> In the case of nonhydrogenated diamondlike carbon films, it has been reported that there are little to no hydrogen present on its surface and in its bulk. Furthermore,

nonhydrogenated diamondlike carbon films have unique characteristics such as high  $sp^3$  content (>85%) leading to superior material properties such as highly dense, high Young's modulus (>760 GPa), high hardness (>60 GPa), wear resistant, chemically inert, and have physical properties approaching that of crystalline diamond.<sup>2</sup> Unlike that of crystalline diamond, one unique feature of these nonhydrogenated films is its extremely smooth surface, with roughness  $R_a < 1$  nm for as-deposited films. These nonhydrogenated diamondlike carbon films have several names and is most commonly known as tetrahedral amorphous carbon (ta-C). It is sometimes referred to as amorphous diamond (*a*-D) or diamondlike amorphous carbon (DL-*a*C) films. In this article, we will use the common name of ta-C to describe these films.

One of the potential material candidates for field emission displays is ta-C. As such, there have been numerous efforts to improve its electron emission properties by various means. Examples include incorporation of metal particles into the ta-C films,<sup>4,5</sup> changing the surface morphology of the films,<sup>6</sup> and inducing the presence of hydrogen into the microstructure.<sup>7-9</sup> In the case of the latter, although a drop in the work function was reported when hydrogen was introduced during the deposition of the ta-C films using the FCVA technique, the hydrogenated ta-C films were found to have less superior material properties more similar to that of hydrogenated diamondlike carbon films previously described.

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In addition, improved electron field emission properties were also reported in similar studies but it was concluded that the improvement was due to an increase in emission site density or chemical termination rather than a significant drop in work function.<sup>7-9</sup>

If the high  $sp^3$  content superior bulk properties of the ta-C films can be maintained, it may lead to many potential applications. This means that any modifications to enhance the electron emission properties of the material can only be limited to the surface. One way to achieve this is through a postdeposition hydrogen plasma treatment process. Hydrogen plasma treatment has been previously reported on high  $sp^2$  content amorphous carbon film where it induced surface modification of the films and better electron emission was observed. However, the enhancement in the electron emission was believed to be due to the increase in surface morphology as hydrogen plasma has been known to preferentially etch  $sp^2$  bonding as compared to  $sp^3$  bonds.<sup>2,10</sup> In this article, a comprehensive understanding into the effects of hydrogen plasma treatment on the surfaces of these films is reported. Using high  $sp^3$  content ta-C films, we will show that hydrogen plasma treatment using microwave plasma does enhance the electron emission of ta-C films by lowering the turn-on field rather than significantly changing the surface morphology. In contrast to previous reports, we will further show that this is mainly due to the formation of surface C-H dipole layer through *in situ* reflection high-energy electron loss spectroscopy (RHEELS) with a significant reduction in the work function using ultraviolet photoelectron spectroscopy (UPS). The stability of the C-H dipole layer is important as an unstable surface will not be useful for device applications. As such, the stability of the hydrogen modified surface will be studied by thermal annealing and *in situ* UPS. Atomic force microscopy (AFM) was also performed to study the surface morphology of the films before and after the hydrogen treatment, and also after thermal annealing.

## II. EXPERIMENTAL DETAILS

High  $sp^3$  content ta-C films were deposited on highly doped  $n++$  Si(100) substrates using a Lambda Physik 248 nm KrF pulsed laser ablation system under high-vacuum conditions of  $1 \times 10^{-6}$  torr. The target used was 99.9% pure carbon and the laser was operating at 20 Hz pulse rate with energy of 200 mJ. After deposition, the ta-C films were then subjected to surface hydrogenation at 500 °C for 1.5 min in a hydrogen microwave plasma systems, operating at 450 W at an operating pressure of 20 mbar. The samples for the photoemission experiments, UPS and x-ray photoelectron spectroscopy (XPS), were transferred *ex situ* into the ultra-high vacuum (UHV) chamber at the SINS beamline<sup>11</sup> of the Singapore Synchrotron Light Source (SSLS), with a base pressure of better than  $1 \times 10^{-10}$  mbar. UPS spectra were recorded at normal emission with photon energy of 60 eV and XPS was performed using x-ray source of 650 eV at a constant pass energy of 20 eV for the narrow scans. In order to correlate the experimental results, the samples were transferred *in situ* into a UHV chamber with a base pressure of  $5 \times 10^{-11}$  mbar for RHEELS measurements.

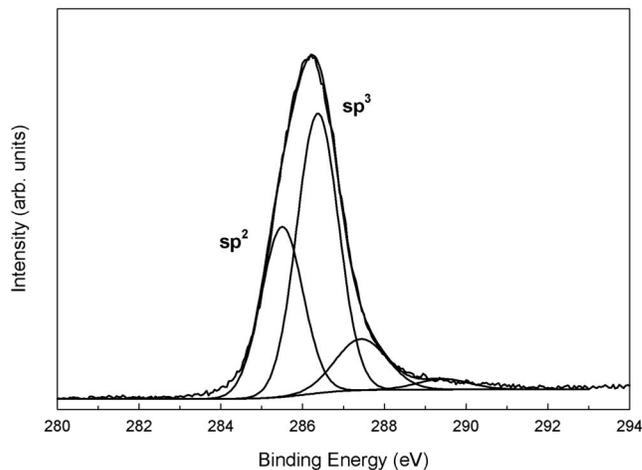


FIG. 1. As received XPS spectra of ta-C films confirming high  $sp^3$  content in the films.

Surface morphology and surface roughness of the specimens were analyzed by AFM in ambient conditions. The images were obtained using a Veeco Nanoscope 3 Multimode AFM operating in tapping mode. AFM images acquired were flattened using the software provided by the manufacturer and not modified by any filtering. The rms roughness was evaluated over an area of  $1 \times 1 \mu\text{m}^2$ . The films were also tested after vacuum annealing at 1000 °C to compare whether any significant morphological changes were present. Vacuum electron emission test of ta-C samples before and after hydrogen plasma treatment was carried out with a custom-designed field emission system, using parallel plate geometry at room temperature. The specimens were loaded into the vacuum chamber and pumped down to a pressure of  $\sim 1 \times 10^{-6}$  torr. The emitter-to-anode distance was maintained at 100  $\mu\text{m}$  by inserting a polymer film spacer, on which a hole with a fixed area was fashioned to define the total emission area. The field emission current-voltage ( $I$ - $V$ ) relationship was obtained by applying a dc field between the sample and anode. Emission current was measured using a Keithley 237 source measurement unit. The leakage current was also measured by reversing the applied voltage.

## III. RESULTS AND DISCUSSION

The ta-C films used in this study were deposited at room temperature with a film thickness of approximately 80 nm. The  $sp^3$  content of the film was analyzed using XPS. As shown in Fig. 1, using two Gaussian peaks at 285.1 and 286.2 eV for peak fitting confirm a high  $sp^3$  content of  $>80\%$  for the as-prepared films. A third peak at 287.6 eV is attributed to ambient C-O oxidation. No sputter etch was performed in order to keep the surface in pristine conditions for UPS measurements. The comparative peak intensities between the  $sp^3$ ,  $sp^2$ , and C-O peaks show that the C-O peaks are much lower in intensity. Other than a small O 1s peak present, no other elements are observed in the survey spectrum (not shown).

After hydrogen plasma treatment, the samples were transferred *ex situ* for RHEELS. Figure 2 shows the

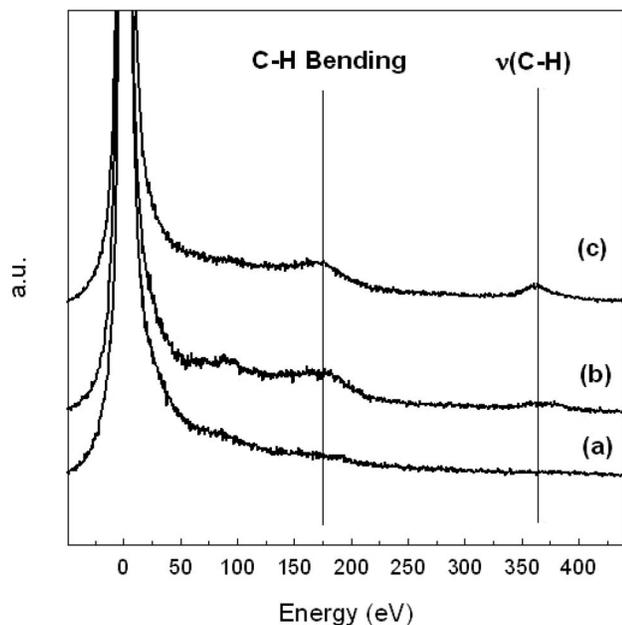


FIG. 2. HREELS spectrum of (a) as-received nonhydrogenated ta-C films, (b) after microwave hydrogen plasma treatment for 30 s, and (c) after microwave hydrogen plasma treatment for 90 s.

RHEELS spectrum where the as received nonhydrogenated ta-C films show a relatively smooth spectrum with no visible energy loss peaks in Fig. 2(a). Figures 2(b) and 2(c) show the spectrum of the specimen after microwave hydrogen plasma treatment for 30 and 90 s, respectively. The presence and increase in peaks at 170 and 360 eV correspond to the C–H bending and vibrational C–H bonds, respectively. This shows that the microwave plasma process is successful in incorporating hydrogen onto the surface carbon atoms. This leads to the formation of a C–H dipole layer and, thus, the presence of a hydrogen-terminated surface.

In order to study the stability of the hydrogen-terminated ta-C films, *in situ* UPS analysis of the films at various annealing temperatures was studied in UHV conditions to ensure no surface oxidation. Figure 3 shows the combined valence band UPS spectra in low kinetic energy cutoff for the as-prepared and hydrogenated films at various annealing temperatures. To eliminate the influence of the analyzer work function, a negative sample bias of 5 V was applied in the measurements. The kinetic energy scale in Fig. 3 was calibrated after the deduction of the applied bias and referenced to the Fermi level of the specimen. An increase in the intensity of the secondary electrons is observed from the as-prepared specimen (filled circles) to the hydrogen treatment specimens (hollow circles). In addition, it is clear that the hydrogen plasma treatment greatly reduced the work function of the ta-C films by about 1 eV from 4.8 to 3.8 eV. Interestingly, during annealing at 300 °C (filled triangle) a further reduction in the work function from 3.8 to 3.6 eV can be observed. It is highly likely that this further reduction at 300 °C can be attributed to the both the removal of H<sub>2</sub>O absorption and ambient oxidation from exposure to air during the specimen transfer to the UHV system. Further increase in the annealing temperature from 300 °C to a high of 600 °C (hollow triangle) shows little change in the work

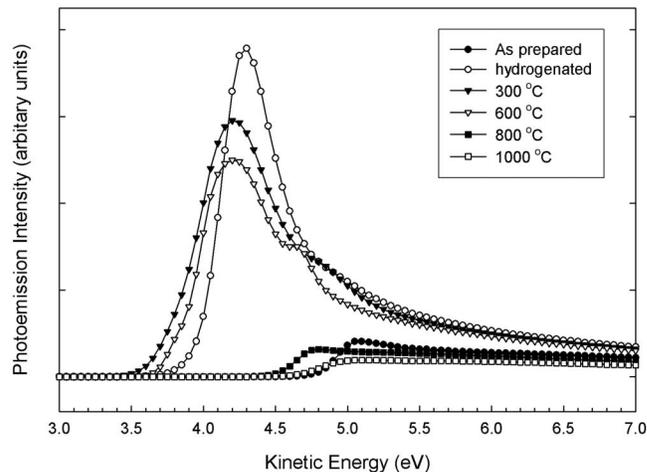


FIG. 3. The low kinetic energy part of the UPS spectra in ta-C films after different treatments: as-prepared (filled circles), hydrogenated (hollow circles), hydrogenated and after annealing at 300 °C (filled triangles), 600 °C (hollow triangles), 800 °C (filled squares), 1000 °C (hollow squares). All spectra were recorded at normal emission with photon energy of 60 eV.

function. At 800 °C (filled squares), a distinct change in both the intensity and work function is observed. The intensity of the secondary electrons drops significantly while the work function jumps to  $\sim 4.5$  eV and upon further increase in the annealing temperature to 1000 °C (hollow squares), the work function appears to revert back to 4.8 eV, which is similar to the as-prepared ta-C films. Furthermore, this revert is also observed in the intensity of the spectrum, where the secondary electron emission intensity units are nearly similar to that of the as-prepared ta-C films.

In Fig. 4, electron emission from ta-C films are shown (a) as prepared, (b) after hydrogen treatment, and (c) after 1000 °C annealing. The effects of hydrogen treatment can be observed where a low turn-on field at about 7.0 V/ $\mu\text{m}$  is obtained. However, the as-prepared ta-C film and the ta-C

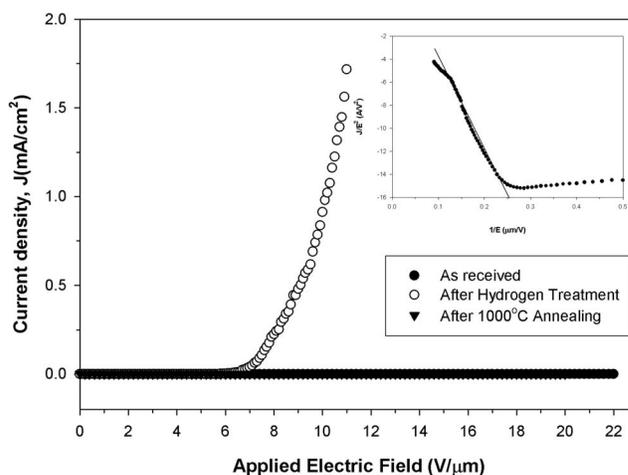


FIG. 4. Field emission current density against applied field for the ta-C films (a) as prepared, (b) after 90 s hydrogen treatment, and (c) after hydrogen plasma and after 1000 °C annealing. No emission current was obtained from as-prepared pristine as well as the after 1000 °C annealed ta-C films. The insert shows the Fowler–Nordheim plot for the electron emission process after 90 s hydrogen treatment, where a linear line can be plotted.

film after 1000 °C annealing did not show any electron emission, even at the maximum electric field using the present experimental setup. This is consistent with the typical turn-on field for ta-C films in the range of 20–40 V/ $\mu\text{m}$  as previously reported.<sup>12</sup> The Fowler–Nordheim plot is shown as insert in Fig. 4. A straight line can be extrapolated which proves that the enhanced emission process is due to field emission and not other types of emission. The change in the work function by 1.0–1.2 eV is much larger than previously reported values of 0.6 (Ref. 9) and 0.1 eV.<sup>10</sup> This larger reduction is largely due to the high  $sp^3$  concentrations (>80%) of the ta-C films deposited by PLD technique as previous reports showed that hydrogen is more likely to bond to a  $sp^3$  site while the  $sp^2$  regions remain unterminated.<sup>9</sup>

AFM analysis is performed in order to study and confirm how significant is the etching effects on the surface morphology of ta-C films after hydrogen microwave plasma treatment. Some researchers have reported that etching effects may affect the electron emission properties due to the fabrication of large spindtlike tips during the etching process.<sup>10</sup> In Fig. 5, the AFM images of surface of ta-C film (a) as prepared, (b) after hydrogen plasma treatment, and (c) after hydrogen plasma treatment and annealing at 1000 °C are shown. The high  $sp^3$  content ta-C specimens clearly show that there are minimal differences in the morphology for all the films, with a mean roughness (Ra) values of (a) 0.19 nm, (b) 0.22 nm, and (c) 0.30 nm, respectively. As the scanned areas for all the specimens are  $1 \times 1 \mu\text{m}^2$  and the height scale is 5 nm as shown, the slight increase in the roughness observed between Figs. 5(a) and 5(b) for as prepared samples and samples after hydrogen plasma are minimal. This rules out the effects of plasma etching as the origin of the enhanced field emission for the hydrogenated film as the short 90 s hydrogen plasma treatment did not create large micron-sized spindtlike tips. Previously, researchers reported that ta-C is stable up to as high as 1100 °C. However, the material properties of ta-C such as optical bandgap start to degrade above 600 °C possibly due to internal microstructural changes.<sup>13–16</sup> After annealing at 1000 °C, it is likely that there is a significant decrease in the  $sp^3$  content of the ta-C films. In spite of this, Fig. 5(c) showed the surface morphology of the ta-C films was not significantly affected, with a small increase in the mean roughness to (Ra) 0.30 nm. However, this increase in the roughness does not correspond to any electron emission as shown in Fig. 4(c). As such, these results show that the surface morphology does not play a significant role in the electron field emission process in this comprehensive study, which instead is due to the C–H bonds created from the hydrogen plasma treatment. Furthermore, there are previous reports which claimed that the hydrogen plasma etching tends to affect  $sp^2$  bonds much more than  $sp^3$  bonds<sup>10</sup> which in this work, our results corroborate with other researchers.

Our results show that hydrogen termination on ta-C films is comparatively stable to those reported on crystalline diamond surfaces.<sup>17</sup> The effects of surface hydrogenation of crystalline diamond films are well known and have been reported as early as 1989.<sup>1,18</sup> Crystalline diamond films are unique as it can undergo  $p$ -type transfer doping by surface

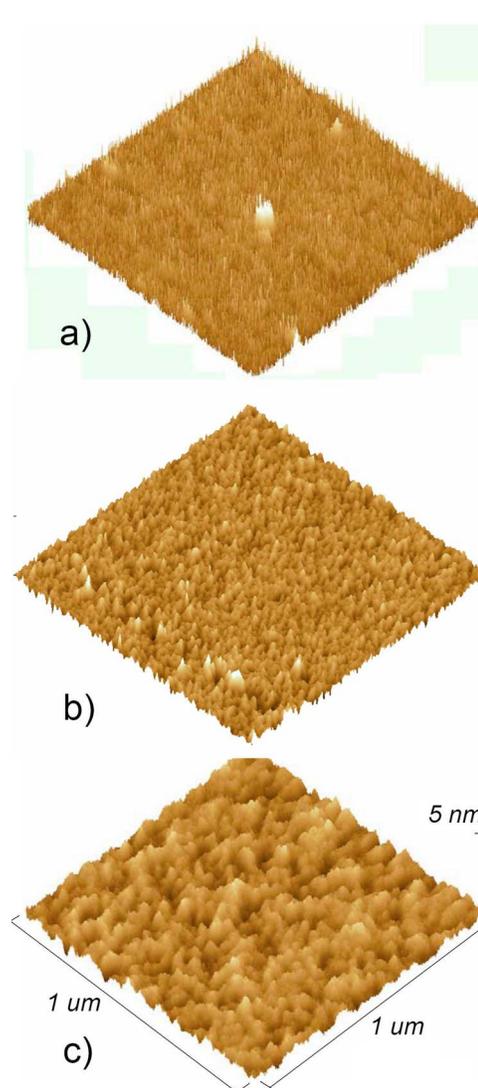


FIG. 5. (Color online) AFM images of surface of ta-C film (a) as prepared, (b) after H plasma treatment, and (c) after H plasma treatment then annealing at 1000 °C. The scanned areas are all  $1 \times 1 \mu\text{m}^2$  and the height scale is 5 nm.

hydrogenation. The main cause is due to the ambient absorption of  $\text{H}_2\text{O}$  which gives rise to  $\text{H}_3\text{O}^+$  bonds on the hydrogen-terminated surface, thus leading to an increase in surface conductivity. At above 200 °C,  $\text{H}_2\text{O}$  desorbs which can result in a reduction in the surface conductivity by as much as four orders of magnitude.<sup>19</sup> However, the C–H dipole of the hydrogen-terminated crystalline diamond surface is stable up to as high as 700 °C.<sup>20</sup> In this article, the hydrogen-terminated ta-C films have similar behavior to previous reports on hydrogenated crystalline diamond films. For example, the formation of C–H dipole layers by hydrogen plasma treatment and the ambient absorption of  $\text{H}_2\text{O}$  by the C–H dipole layers. Likewise, the desorption of  $\text{H}_2\text{O}$  at temperature  $<300$  °C and the stability of C–H bonds at a high of 600 °C for ta-C films are very close to the values reported in hydrogenated crystalline diamond films. This may be expected as both materials have relatively similar properties such high band gap ( $\sim 4.0$  eV for ta-C) and similar types of carbon  $sp^3$  bonds present.<sup>2</sup>

However, hydrogen-terminated ta-C does have its uniqueness. The surface absorbed H<sub>2</sub>O by the C–H dipole layer does not play a significant role in the reduction of the work function. Instead, it actually increases the work function of the ta-C by approximately 0.2 eV which after H<sub>2</sub>O desorption, a lower work function is obtained. The desorption of hydrogen from the surface of the ta-C films may be due to both the activation energy of hydrogen<sup>20</sup> as well as the change in the microstructure of the ta-C films which both have the same temperature range of ~600 °C. In general, hydrogen termination (or C–H surface dipole layer) in ta-C is responsible for reducing the work function which leads to enhanced electron field emission properties. The C–H dipole layer is stable to over 600 °C while showing the same low work function values and enhanced field emission. The stability of the hydrogen surface treated ta-C films over high temperature range is very important for various electron emission device applications.

#### IV. CONCLUSIONS

We have shown that hydrogen plasma treatment on ta-C films prepared by PLD modified the film by creating a hydrogen-terminated surface. This hydrogen termination reduces the turn-on field for electron field emission and is predominantly due to a large decrease of work function by 1.0–1.2 eV. This hydrogen termination on the surface was further proven to be highly stable even under high temperature annealing of up to 600 °C. AFM results showed that the surface morphology of the high *sp*<sup>3</sup> content films was not significantly affected by the hydrogen treatment.

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