Mechanical properties of nanostructured copper/hydrogenated amorphous carbon multilayer films grown in a low base vacuum system

Neeraj Dwivedi[1,2], Sushil Kumar[1,*], Davinder Kaur[2], C. M. S. Rauthan[1], O. S. Panwar[1]

[1]Plasma Processed Materials Group, National Physical Laboratory (CSIR), New Delhi, India-110012, [2] Department of Physics and Centre of Nanotechnology, Indian Institute of Technology, Roorkee, India-247667

Abstract

Nanostructured copper/hydrogenated amorphous carbon (Cu/a-C:H) multilayer films have been deposited in a low base vacuum system (base pressure $1x10^{-3}$ Torr) and studied for their mechanical properties. The analysis shows very low residual stress (below 1 GPa), moderate nanohardness (H) and elastic modulus (E) of the resultant films. Further these films have been studied for their plastic deformation energy and elastic recovery. Atomic force microscopic analysis reveals the nanostructured morphology and low surface roughnesses of the resultant films. Estimated roughnesses values have also been correlated with the experimental measured H values. The presence of Cu in these structures have been confirmed by time of flight-secondary ion mass spectroscopy, X-ray photoelectron spectroscopy and energy dispersive X-ray analysis.

Keywords: Copper/hydrogenated amorphous carbon multilayer, Nanostructure, Nanohardness, Surface roughness

*Corresponding author: E-mail address: skumar@ nplindia.org (Sushil Kumar)

Tel: +91-11-45608650; Fax: 91+11-45609310

Optoelectronics And Advanced Materials-Rapid Communications Volume: 4 Issue: 4 Pages: 604-609 Published: Apr 2010

1. Introduction

Diamond like carbon (a-C:H or DLC) thin films retains considerable scientific and industrial interest due to its low friction and high hardness properties, which result in its applications as a hard and protective coating on magnetic storage devices, micro-electromechemical systems and coating on parts of heart valves [1-3]. However, high level of residual stress exist in DLC films limits its wide-spread applications. Multilayer films are found to be an appropriate approach to minimize the high level of residual stress and improve tribological properties [4, 5]. Voevodin et al. [6, 7] have extensively studied the various architectures of multilayer composite coatings with super hard a-C:H layers for wear protection at high contact loads. The importance of DLC multilayer films has also been reported by Yeldose et al. [8]. Pauleau et al. [9] have broadly studied the Cu containing a-C:H films for their mechanical properties and found very low hardness values (2 to 6 GPa). There are sufficient literature available on metal/DLC such as Ti/DLC multilayer and bilayer films for mechanical applications, but negligible reports has been found throwing light on the mechanical aspect of Cu/a-C:H multilayer films.

In this manuscript, we report the mechanical properties of nanostructured Cu/a-C:H multilayer films grown in a low base vacuum system using combined radio frequency (RF)-plasma enhanced chemical vapor deposition (RF-PECVD) and RF-sputtering techniques. These films exhibited moderate nanohardness (H) and very low residual compressive stress (S). The mean (R_a) and root mean square (R_q) roughnesses values, estimated by atomic force microscope (AFM) technique, have also been correlated with H and elastic modulus (E). The presence of Cu in these multilayer films was confirmed by time of flight-secondary ion mass spectroscopy (TOF-SIMS), x-ray photoelectron spectroscopy (XPS) and energy dispersive x-ray analysis (EDAX).

2. Experimental Details

Four sets of nanostructured Cu/a-C:H multilayer films have been deposited using a hybrid system involving RF-sputtering and RF-PECVD techniques, in the sequence of alternate layers of Cu and a-C:H, on well cleaned silicon wafer, Corning 7059 glass, stainless steel sheet, substrates. Prior to multilayer film deposition, the substrates has been cleaned for 10 min in RF argon (Ar) plasma at a high negative self bias voltage of about 300 V. The ultimate base pressure for deposition was $\sim 1\text{x}10^{-3}$ Torr in all the processes that has been achieved by a root blower pump backed by rotary pump. A Cu disk of 50 mm diameter has been used as the metal sputtering target and the substrate to metal target distance has been kept constant to about 6 cm. All depositions has been carried out at constant negative self biases of 300 and 100 V for RF-sputtering and RF-PECVD processes, respectively, at constant Ar and acetylene (C_2H_2) gas pressures of 70 mTorr and 28 mTorr, respectively. Only the number of Cu/a-C:H bilayers (combination of one Cu and one a-C:H layer makes one Cu/a-C:H bilayer) has been changed from 1 to 4. During Cu layer deposition, the electrode on which the substrates have been placed is connected to ground and RF power has been applied to target electrode, while during a-C:H deposition, target electrode has been connected to ground and RF power has been applied to electrode on which substrates are placed.

Using a laser scanning curvature method, the S of the multilayer films at room temperature has been estimated by a Frontier semiconductor 500 TC stress measurement system. TOF-SIMS measurement has been performed using ion TOF-SIMS instrument to find out the elemental composition of these multilayer films. This instrument equipped with Bi-cluster ion analysis gun and sputter O_2 gun. Similarly, EDAX has been used to identify the presence of Cu and carbon in the deposited structures. XPS spectra of these films have been obtained by Perkin Elmer 1257 instruments using X-ray radiation of Al K_α 1486.6 eV. AFM analysis has been done using Veeco V Nanoscope instrument.

3. Result and Discussions

3.1 TOF-SIMS

Fig.1 shows the TOF-SIMS depth profiles for Cu, C, O and Si from Cu/a-C:H multilayer film having 4 Cu/a-C:H bilayers. The solid, dash, dot and bold solid lines represent the elements namely, C, Cu, O and Si, respectively. This is to be noted that this multilayer film consists of 4 Cu and 4 a-C:H layer, alternatively. TOF-SIMS analysis gives a clear elemental demarcation between Cu and a-C:H layers. Figure clearly shows the 4 steps of Cu within the certain intervals, which evident the existence of 4 Cu layer in the structures. It can be seen that, in comparison to that of Cu, no steps has been observed for C. This may be due to (i) TOF-SIMS technique is very sensitive for metals like Cu and (ii) the hydrocarbon plasma always dominant in deposition system therefore, even during the growth of Cu layer, some carbon atoms travel in processing chamber and may be condensed over the growing structures. The TOF-SIMS depth profile also reveals the presence of significant amount of O in depth of this structure because of their high base pressure ($1x10^{-3}$ Torr) depositions. At this high base pressure, sufficient air is diluted in the multilayer structures. However, very high intensity Si peak has been accounted to the fact that Si substrate has been used for the growth of these multilayer films.

3.2 XPS & EDAX

XPS has been used to investigate the chemical composition, oxidation state and structural properties of Cu / a-C:H multilayer films and the deconvoluted C 1s spectra for 4 Cu / a-C:H bilayers film has been shown in Fig.2 (a). The spectra fitted with three peaks obtained at 284.2, 285.2 and 286.8 eV has been assigned to sp^2 C, sp^3 C and C-O bondings, respectively. The FWHM values for these peaks were found to be 1.7, 1.7 and 2.2 eV, respectively. Similarly, the area under the curve for peaks at 284.2, 285.2 and 286.8 eV was found to be 63.6, 23.2 and 13.2 %, respectively. In view of all these, it is found that these multilayer films have more graphite-like nature. Further, graphite-like nature of these films have also been confirmed by mechanical properties which show moderate values of H and E as discussed in other section. It is interesting to note that the Cu layer is covered under the a-C:H layer. Therefore, this multilayer film has been sputtered for 5 minutes to visualize the presence of Cu in the structure. The 5 minute sputtered Cu (2p) core level spectra of Cu / a-C:H multilayer structure having 4 bilayers is shown in Fig.2 (b). Spectra reveal the presence of two intense peaks centered at 932.9 and 952.4 eV. It is to be noted that the binding energy of Cu ($2P_{3/2}$) is shifted to higher values comparison to that of pure Cu peak, suggest the contribution of CuO. The Fig.2 (c) shows the O 1s core level spectra of same sample. The presence of O (1s) peak in the spectra may be attributed to two facts: (i) deposition of these multilayer structures took place at comparatively high base pressure of the order of 1×10^{-3} Torr, which allowed some air dilution in the structures during its growth and (ii) prior to XPS measurements, the samples has been exposed in ambient air which led to surface contaminations. The oxygen plasma may be very useful in Cu / a-C:H multilayer structures for improving mechanical properties. Jiang et al. [10] have already reported that oxygen plasma preferentially etches the soft graphitic like sp^2 clusters and enhanced the diamond-like character.

EDAX measurement was performed to investigate the composition of Cu/a-C:H multilayer film. EDAX spectra of Cu/a-C:H multilayer film having 4 bilayers is demonstrated in Fig.3. It can be seen from the figure that in addition to strong C and lower intensity Cu peaks, strong Si and O peaks have also been observed. Si peak arises from the substrate whereas the O peak appears due to the high base pressure of 1×10^{-3} Torr used in the growth of these films which is also evidenced by XPS results. Gold (Au) peak is also obtained in the spectra, since substrates were Au sputtered to make contact during SEM and EDAX measurements.

3.3 AFM

Surface morphology of Cu/a-C:H multilayer film having 1 and 4 Cu/a-C:H bilayers, studied by AFM, are presented in Fig.4. In contrast to pure a-C:H [11], these images reveal the nanostructured surface morphology with particle size of 45 and 55 nm for films having 1 and 4 Cu/a-C:H bilayers, respectively. It is expected that these nano-particles are of carbon since the top layer is of a-C:H itself. Note that carbon nanotubes and nanofiber structures also require a very thin base layer of metal prior to deposition. Further, R_a and R_q roughnesses in these multilayer structures were found to be very low. The structure having 1 Cu/a-C:H bilayer shows R_a and R_q values of 0.37 and 0.53 nm, respectively. However, with increase in interfacial states these roughnesses have been increases and found to be 0.73 and 0.92 nm, respectively for structure having 4 Cu/a-C:H bilayer.

3.4 Mechanical properties

Nanostructured Cu/a-C:H multilayer, in which Cu and a-C:H layers are stacked on top of one another, has been prepared to obtain low residual compressive stress (S) films. Fig.5 shows the variation of S versus number of Cu/a-C:H bilayers. It is evident from figure that initially S increases with increasing Cu/a-C:H bilayers but beyond certain number of bilayers it starts to decrease. The films having 1, 2 and 3 Cu/a-C:H bilayers exhibited S as 0.5, 0.7 and 0.85 GPa, respectively. However, structure having 4 Cu / a-C:H bilayers exhibit S of 0.75 GPa. This is to be noted that S in all the multilayer films studied is below 1 GPa. The concept of soft/hard layer is used here for minimizing the S values. Thin soft Cu layer grown using RF-sputtering technique are interface layers and acts as an adhesive layer for RF-PECVD grown hard a-C:H layer. It appears that one can obtain thick DLC films with a multilayer structure of Cu/a-C:H, because interface layers present in the multilayer structures reduce the S in films as soft/hard structure provides the needed relaxation in the overall structure. The pulsed plasma grown soft / hard DLC layer and Si containing DLC multilayer structure concepts for the relaxation of S have been reported by Kumar et.al [12, 13]. Moreover, the soft Cu layer present in the multilayer structure acts as a metallic substrate for subsequent a-C:H layers and therefore, prevents the delamination.

Nanoindentation is found to be very suitable technique to study the mechanical properties at nanoscale. Fig.6 (a) and (b) shows the variation of H and E versus number of Cu/a-C:H bilayers. The values of H and E has been found to be in the range of 13 to 6 and 177 to 100 GPa, respectively depending upon number of Cu/a-C:H bilayers. This can be seen that the maximum values of H and E has been observed for the structure having only 1 Cu/a-C:H bilayer, that decreases further on increasing Cu/a-C:H bilayers. The reduction in these values with increase in Cu/a-C:H bilayer is may be due to an increase of number of interfacial states. Reduction in H and E values may also be explained on the basis that since the deposition of these multilayer films have been carried out at high base pressure of $1x10^{-3}$ Torr and after deposition of each Cu layer, the RF power is made to switch off and then a-C:H layer is allowed to grow, therefore, during off period of RF power, some air bubbles may trap between the region of Cu and a-C:H layers, which may give rise imperfection between these two layers and finally may makes overall structure loosely bound. XPS spectra (Fig. 2) also reveal the shifting of pure Cu peak due to O interference. H and E values have also been known to correlate with sp^3 and sp^2 bondings. The a-C:H films can be divided into three categories, namely (i) more diamond-like (high H); when it contain high sp^3 fraction, (ii) more graphite-like (variation of H between low to moderate values); when it contain high sp^2 fraction and (iii) polymer-like; when these films become very soft and contains significant hydrogen in the structure. It appears that increase in Cu / a-C:H bilayers give rise to more graphite-like sp^2 bonding and therefore, reduces the H and E values. Ji et al. [14] have also suggested the increase in sp^2 bonding with the introduction of Mo in DLC matrix. H and E are also correlated with surface roughnesses values. The structure having low R_a and R_q values (0.37 and 0.53 nm) shows maximum H and E (13 and 177 GPa) than that of structure having high R_a and R_q values (0.73 and 0.92 nm) which shows low H and E (6 and 100 GPa) values. Further, the moderate values of H and E have also been related to elastic recovery (ER). The value of ER is found to be in the moderate range between 47.4 to 57.6 %. Pauleau et al. [9] have observed polymer-like nature in the nanostructured copper/hydrogenated amorphous carbon films due to low H values in their films. Plastic deformation energy (U_r) is also very important concept to describe the mechanical properties [15]. Fig.6 (c) shows the variation of U_r versus number of Cu / a-C:H bilayers. The U_r varies inversely proportional to the H [15]. The values of U_r are found to be in the range from 3.7×10^{-5} to 5.5×10^{-5} joule for multilayer films having number of Cu / a-C:H bilayers between1 and 4. This is to be noted that brittle material exhibit lower U_r while ductile material exhibit comparatively higher U_r. However, observed moderate values of U_r, which increases with increasing Cu / a-C:H bilayers, shows the transition of material from brittle to ductile phase.

4. Conclusions

Nanostructured Cu/a-C:H multilayer films have been deposited using combined techniques, involving RF-sputtering and RF-PECVD, in a low base vacuum system. TOF-SIMS, XPS and EDAX techniques confirm the presence of Cu in these films. AFM analysis reveals the nanostructured surface morphology with particle size of 45 and 55 nm for structure having 1 and 4 Cu/a-C:H bilayers, respectively. AFM technique also provides R_a and R_q roughnesses which is found to be very low and correlated with mechanical properties. S in these structures is found to be well below 1 GPa. These structures exhibited moderate values of H and E values due to its more graphite-like nature. The H and E values decreases with increasing interfacial states and also decreases with increasing surface roughnesses values.

5. Acknowledgment

The authors are grateful to the Director, National Physical Laboratory, New Delhi (India) for his kind permission to publish this paper. Authors also wish to thank Dr. B. R. Chakraborty and Dr. Govind for providing SIMS and XPS measurements facilities, respectively. This research is sponsored by CSIR, Govt. of India, through the Network Project NWP-0027.

References

[1] L. Huang, Y. Hung, S. Chang, IEEE transactions on Magnetics **33**, 4551 (1997).

[2] C. W. Chen, J. Robertson, Diamond Relat. Mater.**15**, 936 (2006).

[3] F. Q. Y. X. Leng, H. Sun, N. Huang, IEEE Transactions on Plasma Science **37**, 1136 (2009).

[4] X. Han, J. Zhu, J. Han, M. Tan, W. Gao, Appl. Phys. A **91**, 529 (2008).

[5] W. Zhang, A. Tanaka, B. S. Xu, Y. Koga, Diamond Relat. Mater. **14**, 1361 (2005).

[6] A. A. Voevodin, S. D. Walck, J. S. Zabinski, Wear **203-204**, 516 (1997).

[7] A. A. Voevodin, J. S. Zabinski, C. Muratore, Tsinghua Sci. Technol. **10**, 665 (2005).

[8] B. C. Yeldose, B. Ramamoorthy, Int. J. Adv. Manuf. Technol. **38**, 705 (2008).

[9] Y. Pauleau, F. Thiery, V. V. Uglov, A. K. Kuleshov, S. N. Dub, M. P. Samtsov, Rev. Adv. Mater. Sci. **4**, 139 (2003).

[10] L. Jiang, A. G. Fitzgerald, M. J. Rose, R. Cheung, B. Rong, E. V. Drift, Appl. Surf. Sci. **1993,** 144 (2002).

[11] D. Sarangi, O. S. Panwar, S. Kumar, R. Bhattacharyya, J. Vac. Sci. Technol. A **18**, 2302 (2000).

[12] S. Kumar, P. N. Dixit, D. Sarangi, R. Bhattacharyya, J. Appl. Phys. **85**, 3866 (1999).

[13] S. Kumar, N. Goyal, P. N. Dixit, C. M. S. Rauthan, Proc. Of the 51st SVC Annual Technical Conference Chicago, page 722 (2008).

[14] L. Ji, H. Li, F. Zhao, J. Chen, H. Zhou, Diamond Relat. Mater. **17**, 1949 (2008).

[15] M. Sakai, Acta Metal Mater. **41**, 1751 (1993).

Figure Captions

Fig.1: TOF-SIMS depth profiles for Cu / a-C:H multilayer structure having 4 Cu / a-C:H bilayers.

Fig.2: XPS core level spectra of (a) C 1s (b) Cu 2p and (c) O 1s for multilayer structure having 4 Cu / a-C:H bilayers.

Fig.3: EDAX spectra of multilayer structure consisting of 4 Cu / a-C:H bilayers.

Fig.4: AFM pictures of multilayer structures having (a) 1 Cu / a-C:H bilayer and (b) 4 Cu / a-C:H bilayers.

Fig.5: Variation of residual compressive stress versus number of Cu / a-C:H bilayers.

Fig.6: Variation of number of Cu / a-C:H bilayers versus (a) H (b) E and (c) U_r.

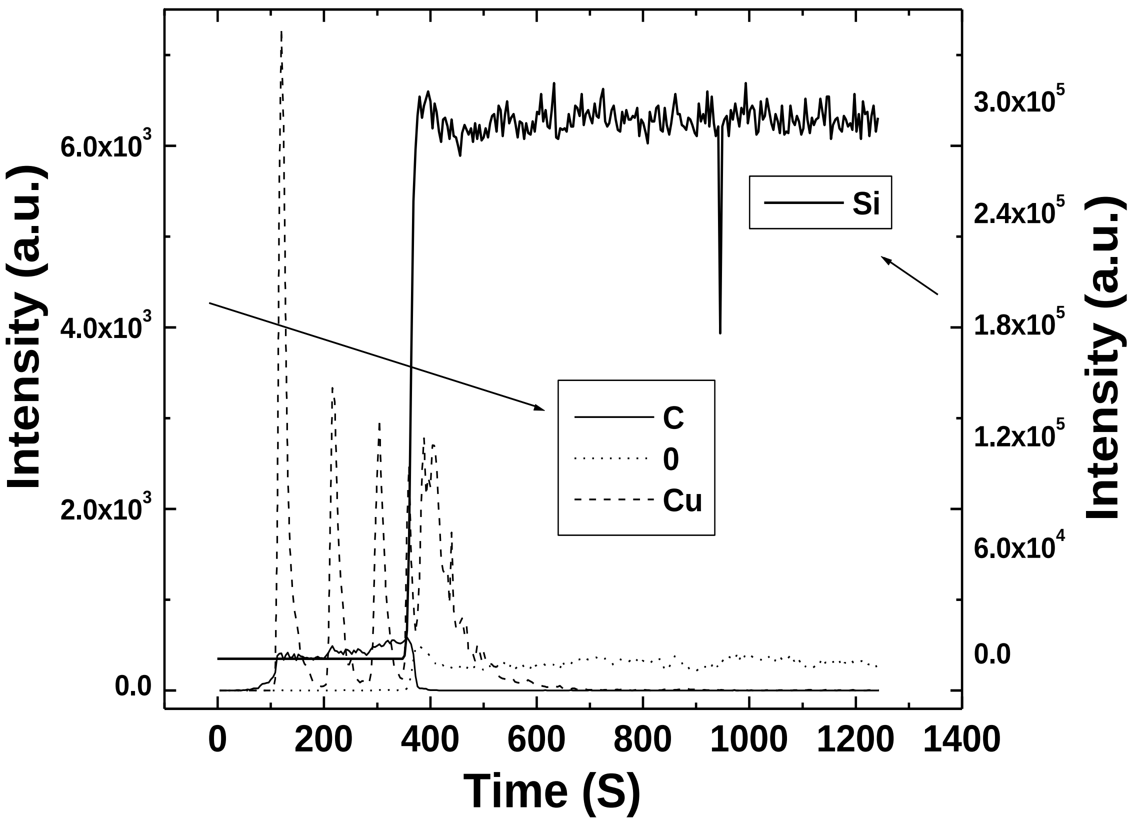

Intensity (a.u.)
6.0x10^3
4.0x10^3
2.0x10^3
0.0
3.0x10^5
2.4x10^5
1.8x10^5
1.2x10^5
6.0x10^4
0.0
Intensity (a.u.)
Si
C
0
Cu
0
200
400
600
800
1000
1200
1400
Time (S)

Fig.1

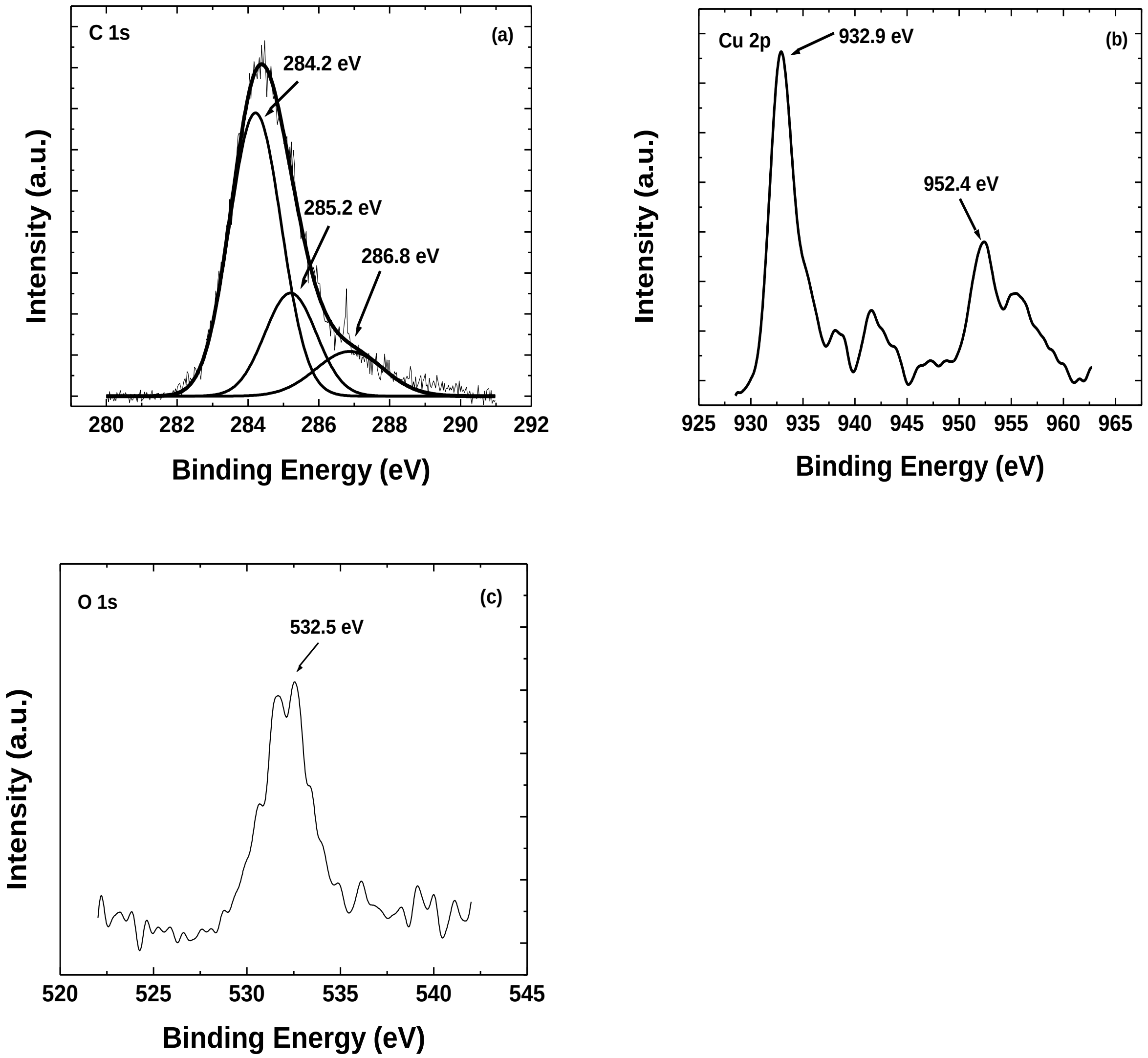

C 1s
(a)
284.2 eV
285.2 eV
286.8 eV
Intensity (a.u.)
280
282
284
286
288
290
292
Binding Energy (eV)
Cu 2p
932.9 eV
(b)
952.4 eV
Intensity (a.u.)
925
930
935
940
945
950
955
960
965
Binding Energy (eV)
O 1s
(c)
532.5 eV
Intensity (a.u.)
520
525
530
535
540
545
Binding Energy (eV)

Fig.2

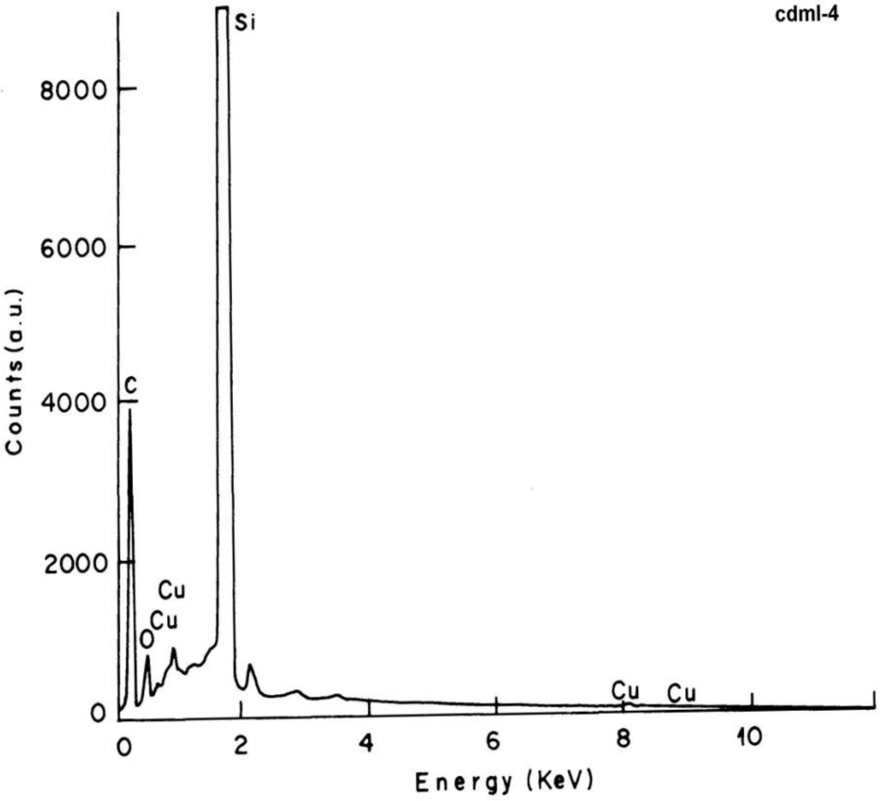
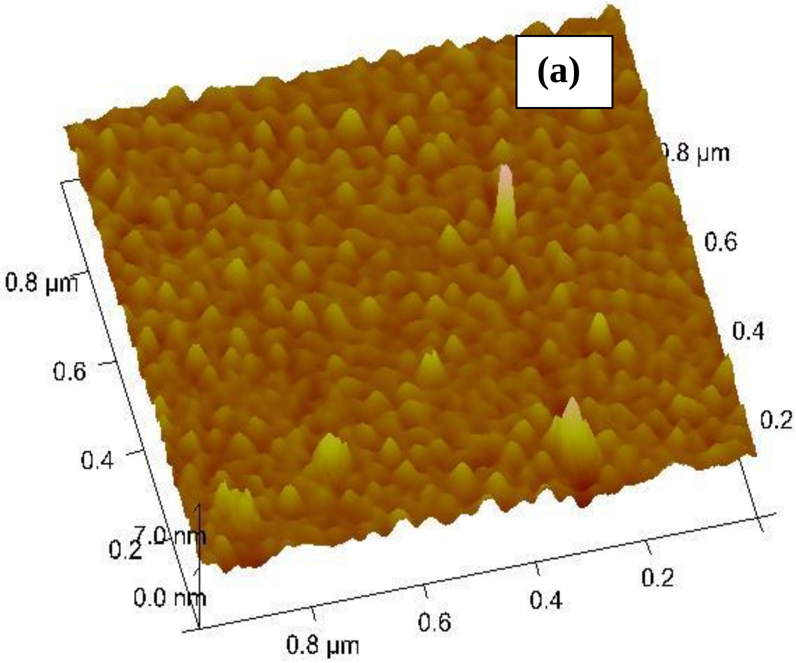
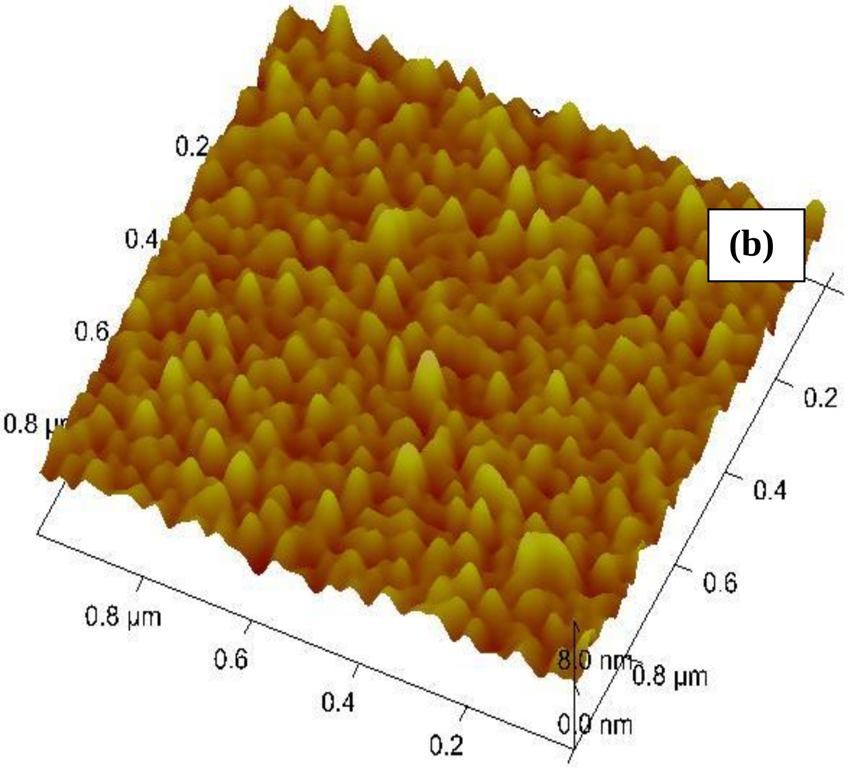

cdml-4
Si
C
O
Cu
Cu
Cu
Cu
Counts (a.u.)
8000
6000
4000
2000
0
0
2
4
6
8
10
Energy (KeV)

Fig.3


(a)
0.8 µm
0.6
0.4
0.2
0.8 µm
0.6
0.4
0.2
7.0 nm
0.0 nm
0.8 µm
0.6
0.4
0.2


(b)
0.2
0.4
0.6
0.8 µm
0.2
0.4
0.6
0.8 µm
8.0 nm
0.0 nm
0.8 µm
0.6
0.4
0.2

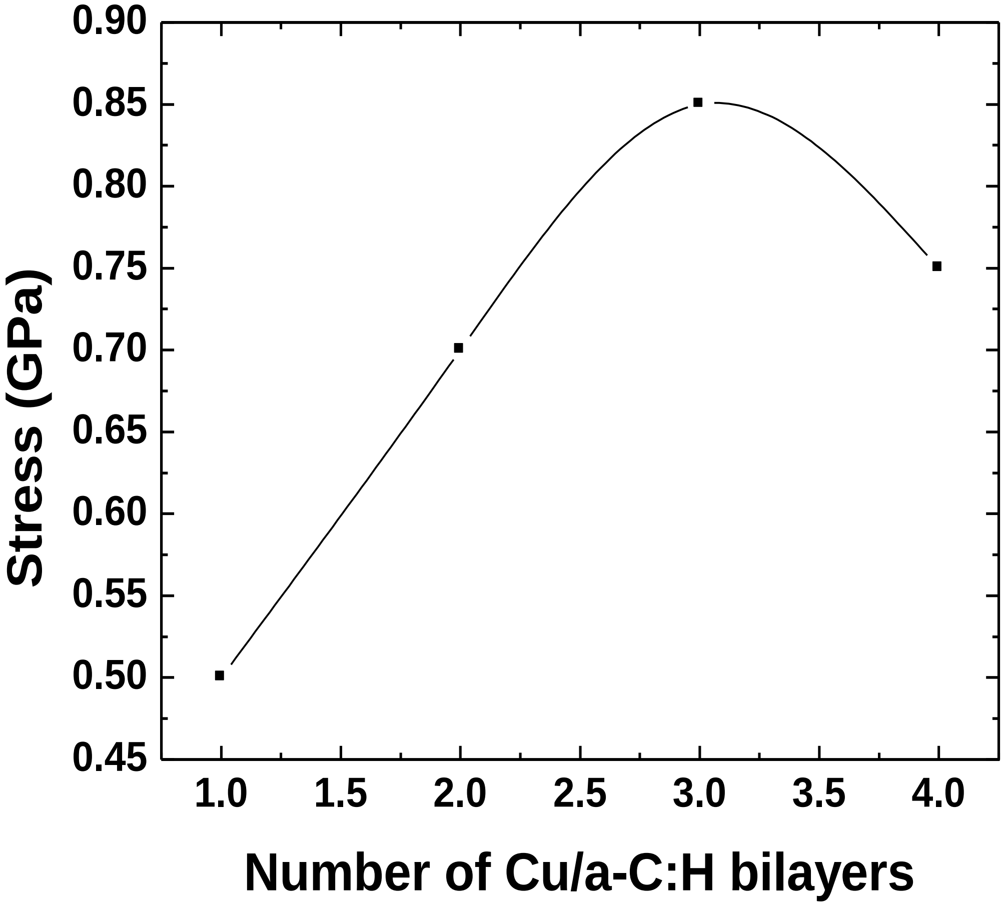

0.90
0.85
0.80
0.75
0.70
0.65
0.60
0.55
0.50
0.45
Stress (GPa)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Number of Cu/a-C:H bilayers

Fig.5

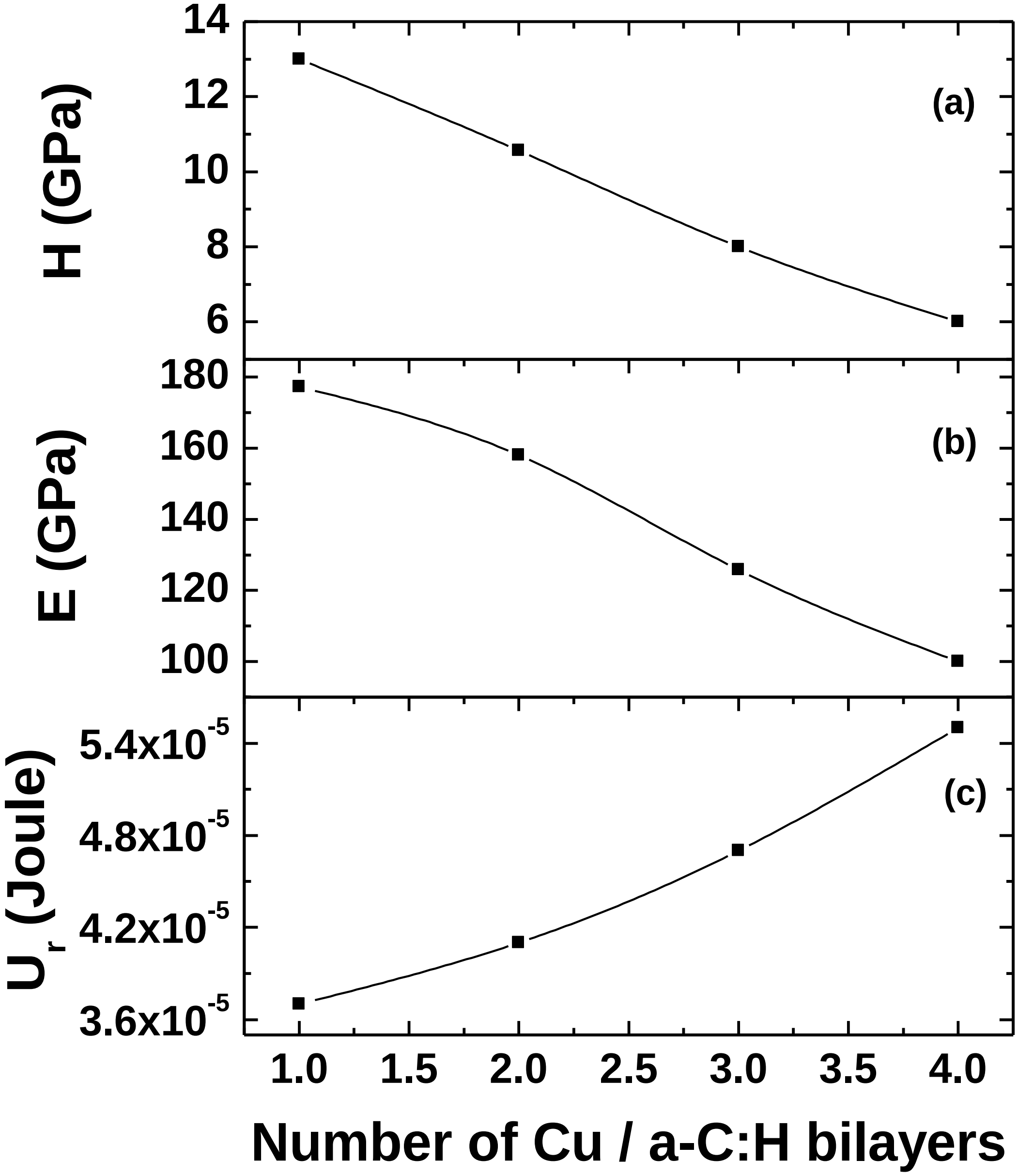

H (GPa)
14
12
10
8
6
(a)
E (GPa)
180
160
140
120
100
(b)
U_r (Joule)
$5.4x10^{-5}$
$4.8x10^{-5}$
$4.2x10^{-5}$
$3.6x10^{-5}$
(c)
1.0
1.5
2.0
2.5
3.0
3.5
4.0
Number of Cu / a-C:H bilayers

Fig.6