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Electrical transport in metal–carbon hybrid multijunction devices

Neeraj Dwivedi [a,b,1], Sushil Kumar [a,*], J. David Carey [c,d], Hitendra K. Malik [b]

[a] National Physical Laboratory (CSIR), K.S. Krishnan Road, New Delhi 110 012, India
[b] Department of Physics, Indian Institute of Technology Delhi, New Delhi 110 016, India
[c] Advanced Technology Institute, University of Surrey, Guildford, GU2 7XH Surrey, United Kingdom
[d] Department of Electronic Engineering, University of Surrey, Guildford GU2 7XH, Surrey, United Kingdom

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ABSTRACT

Understanding the factors that influence the structural, mechanical and electrical properties of hybrid metal–carbon multilayer materials and devices are explored in this study by examining the effects of the choice of metal, Cu or Ti, and the number of metal–carbon bilayers. With up to four bilayers, corresponding to ten discrete metal–carbon electrical junctions, lower interfacial stresses and lower electrical resistance are always found in Cu multilayer structures, when compared with Ti containing multilayers. The lower electrical resistance is a result of a copper–carbon interaction which facilitates a carbon sp^3 to sp^2 bonding transformation and is accompanied by a metal-induced transformation of the carbon layer from an amorphous to nanostructured morphology which also aids in conduction. Time-of-flight secondary ion mass spectrometry measurements demonstrate that the two selected metals, Cu and Ti, represent extreme examples in their affinity to bond with carbon with Cu (Ti) representing a weak (strong) affinity metal for bonding. This study shows the importance of the metal–carbon interaction in understanding the mechanical stresses and electrical characteristics in particular, and the wider result of the role played by the relative chemical reactivity of the components in multijunction hybrid semiconductor-based devices in general.

1. Introduction

Carbon based multilayer structures span the range from semi-metallic graphene-hBN based tunnelling devices [1], graphene and carbon nanotube devices for flexible and transparent electronics [2] to mixed sp^2 and sp^3 amorphous materials. Metal–diamond-like carbon (DLC) hybrid thin film structures have been shown that they can be used for stretchable electronics by employing gold [3], and the inclusion of tungsten is known to improve their mechanical properties, friction and reduce wear [4]. Amorphous carbon (a-C) thin films, and their hydrogenated form, a-C:H, have several advantages over other carbon based materials, such as graphene, nanotubes or diamond, as their intrinsic mechanical and electrical properties can be readily changed by varying the deposition conditions [5,6] without the need for post-deposition chemical surface functionalization and/or material processing. Thin film deposition on substrates, such as silicon or close-packed metals, can affect the amount of interfacial stress and influence the overall electrical transport properties. For example, Godet et al. [7] have developed descriptions of the transport mechanisms through a-C:H and modified a-C:H films, and more recently, the electronic conductivity of a-C:H thin films can be increased through the various inclusions of Ni–Cr dots [8] and via the inclusion of nitrogen dopant atoms [9]. Furthermore, in the area of high field electrical transport, we have previously been able to reduce the threshold electric field for the onset of cold electron emission from DLC films by nanostructuring the surface [10] using a combination of silver micron-sized dots with nitrogen incorporation [11], and alternatively, by employing a copper metal interlayer [12]. When in direct contact with metal, a-C films have also shown a metal-insulator (M-I) transition [13,14] in which the metal-amorphous carbon structure can be efficiently used for switching applications opening up the possibility of use as memory storage devices.

Most electrical transport studies of a-C based materials to date have concentrated on single junction based a-C or a-C:H devices. For example, Miyajima et al. [15] have examined single a-C/*n*-Si heterojunction devices and Hao et al. [16] have fabricated *p*-C/*n*-Si and Fe-C/*n*-Si heterostructure devices. These latter studies have employed single metal layers; what is unknown is how both the interfacial stress and conduction properties change in metal–carbon multilayer device architectures. Multiple electrical junctions, where metal and semiconducting/insulating layers are alternatively used, represent an attractive alternative to single junction devices and are routinely used, for example, in tandem solar cells. Such metal-insulator based multiple junction hybrid devices may demonstrate improved electrical characteristics, such as increases in conductivity, without the need of complex ultrathin layers, and in the case of large area carbon based materials may be readily produced using conventional commercial chemical vapor deposition

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* Corresponding author. Tel.: +91 11 45608650; fax: +91 11 45609310.
E-mail addresses: neerajdwivedi6@gmail.com (N. Dwivedi), skumar@nplindia.org (S. Kumar).

[1] Present Address: Department of Electrical and Computer Engineering, National University of Singapore, Singapore.

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(CVD) systems. In the present study, we investigate the mechanical interfacial stress and electrical transport characteristics of metal/a-C:H device multilayer structures by choosing the two metals, copper and titanium. We explore how increasing the number of alternating metal and a-C:H layers influences the electrical conduction in multijunction devices and demonstrate how the introduction of even a single metal layer increases the conductivity of a-C:H based devices. Amorphous carbon films are also known to usually have high intrinsic stress; while the addition of hydrogen lowers this stress it is often accompanied by an increased sp^3 fraction, with the net effect of an overall lower conductivity. The insertion of thin metal layers helps to lower the overall stress in the film without the need for increased H content and can result in improvements to the overall hybrid structure conductivity and film adhesion. The manuscript shows that the choice of metal plays an important role with differing behaviour between carbide and non-carbide forming metals. Copper as a representative non-carbide metal results in lower measured film stress with better adhesion and increased conductivity when compared to Ti, which is a carbide forming metal.

2. Experimental details

Multilayer films of Cu/a-C:H (Ti/a-C:H) were grown in an alternate sequence of Cu and a-C:H (Ti and a-C:H) layers on well-cleaned *n*-type silicon wafers, as well as on Corning 7059 glass substrates for optical characterization. Deposition occurred at a base pressure of 10^{-3} Torr in a hybrid system combining radio-frequency plasma enhanced chemical vapor deposition (RF-PECVD) and RF-sputtering techniques. High purity Cu or Ti discs of 50 mm diameter were used as sputtering targets and the target to substrate distance was kept at about 6 cm. The metal layers in the multilayer structures were deposited by sputtering at a constant negative self-bias of 300 V in an Ar atmosphere of 70 mTorr pressure. The a-C:H layers were deposited by PECVD on successive metal layers at a constant negative self-bias of 100 V in an atmosphere of C_2H_2 at 28 mTorr. The number of Cu/a-C:H (Ti/a-C:H) bilayers was varied from one to four, where a combination of one Cu (Ti) and one a-C:H layer forms a Cu (Ti)/a-C:H bilayer. Samples C-1, C-2, C-3 and C-4 (T-1, T-2, T-3 and T-4) were prepared using 1, 2, 3 and 4 bilayers of Cu/a-C:H (Ti/a-C:H), respectively, on *n*-Si wafers. Samples C-1G, C-2G, C-3G and C-4G (T-1G, T-2G, T-3G and T-4G) were prepared using 1, 2, 3 and 4 bilayers of Cu/a-C:H (Ti/a-C:H), respectively, on glass substrates [17]. The total thickness of the Cu/Ti and DLC layers of samples C-1, C-2, C-3 and C-4 (T-1, T-2, T-3 and T-4) was measured to be 56, 105, 154 and 205 nm, respectively (227, 277, 312 and 364 nm, respectively). The thickness of the Cu layers and Ti layers was kept at around 15 nm and around 20 nm, respectively. The thickness of each DLC layer was between 36 and 41 nm for the Cu/DLC films. However, the thickness of the first DLC layer for Ti/DLC films was kept at around 207 nm (sample T-1 possessed DLC thickness ~ 207 nm); the thickness of the second, third and fourth DLC layers was varied between 23 and 30 nm.

The residual stress of these multilayer samples was estimated using the change in radius of curvature method by a 500TC temperature controlled film stress measurement system (FSM Frontier Semiconductor, USA). The depth profile of these multilayer samples was analysed by time-of-flight secondary ion mass spectrometry (TOF-SIMS) from ION-TOF GmbH, Germany. For analysis, secondary ions were generated by bombarding pulsed primary ions from a Bi^+ liquid metal ion gun. The overall depth resolution during TOF-SIMS analysis was estimated to be 1 nm. The electrical contacts were made in a sandwich device configuration with Al, produced by thermal evaporation, serving as the top and bottom electrodes. Current–voltage (I–V) characteristics were recorded by varying the voltage from 0 to 10 V using a Keithley 4200 instrument. Structural information was found through scanning electron microscopy. Fig. 1 shows a schematic of the Cu/a-C:H and Ti/a-C:H devices grown on a Si substrate with Al as electrodes. Since Cu/a-C:H and Ti/a-C:H multilayer structures have several metallic Cu and Ti interlayers, they generate several serially connected local junctions between the two electrodes. As shown schematically in Fig. 1, metal–semiconductor–metal (MSM) structures, metal–insulator–metal (MIM) structures, metal–semiconductor (M–S) junction, and M–I junction with several junctions, are present. Devices C-1, C-2, C-3 and C-4 (T-1, T-2, T-3 and T-4) possess a total number of 4, 6, 8 and 10 electrical junctions, respectively, as summarised in Table 1.

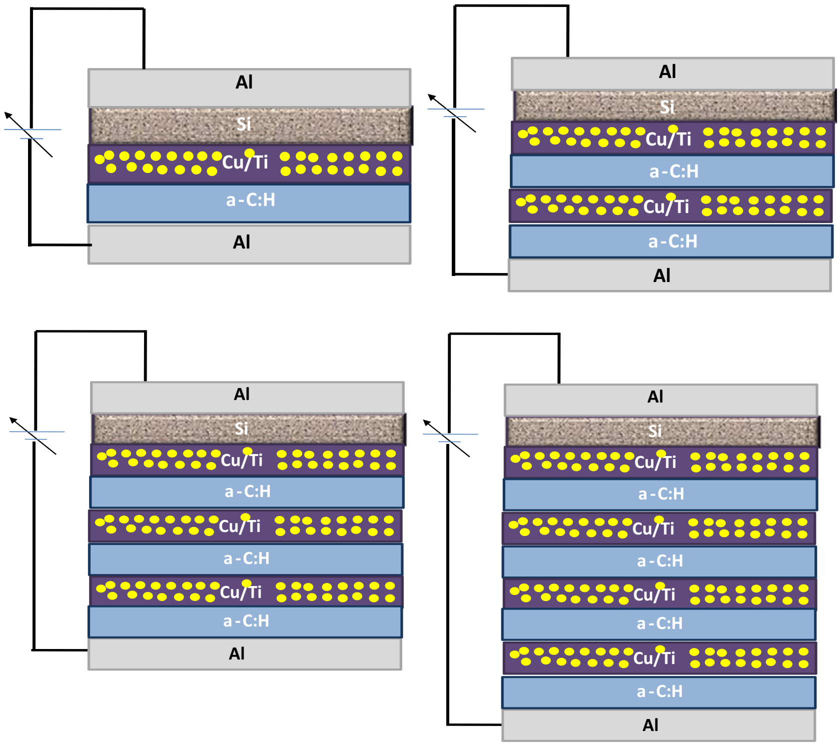

Fig. 1. Schematic representation of hybrid Cu/a-C:H and Ti/a-C:H multijunction devices with electrical contacts used for current–voltage measurements.