Carbon 122 (2017) 336–343

Contents lists available at ScienceDirect

Carbon

journal homepage: www.elsevier.com/locate/carbon

Synthesis and characterization of copper-nanocarbon films with enhanced stability

Romaine A. Isaacs [a], H.M. Iftekhar Jaim [a], Daniel P. Cole [b], Karen Gaskell [c], Oded Rabin [a, d], Lourdes G. Salamanca-Riba [a, *]

[a] Department of Materials Science and Engineering, University of Maryland, College Park, MD, USA
[b] Army Research Laboratory, Aberdeen Proving Ground, Adelphi, MD, USA
[c] Department of Chemistry and Biochemistry, University of Maryland, College Park, MD, USA
[d] Institute for Research in Electronics and Applied Physics, University of Maryland, College Park, MD, USA

ARTICLE INFO

Article history:
Received 21 March 2017
Received in revised form
30 May 2017
Accepted 19 June 2017
Available online 21 June 2017

Keywords:
Copper
Carbon
Covetics
Transparent
Electrode

ABSTRACT

Copper-nanocarbon, called covetic, films made using pulsed laser deposition (PLD) from a target containing nominally 4 wt% carbon in the copper matrix show uniform integration of up to 4.1±0.2 wt.% C. We observe evidence of sp^2 carbon in PLD Cu covetic films in XPS and a peak in the C K-edge in electron energy loss spectroscopy indicative of transitions from the 1s to π^* anti-bonding unoccupied state, suggesting that the C incorporated in the film is graphitic in nature. We measure sheet resistance of 1.7 Ohm/sq and transmittance of 25% at 550 nm in a ≈27 nm thick PLD Cu covetic film after deposition. These films also show much reduced oxidation by scanning probe techniques and very stable resistance for over 120 days - significantly longer than e-beam films of the same thickness. Cu covetic films made by PLD show good promise as transparent electrodes.

1. Introduction

Copper (Cu) has been an industry standard in many electrical and thermal applications, such as bonding wires and as interconnects, but many problems persist and as such has been a topic of considerable interest for some time [1–3]. More recently, Cu is being used as a transparent electrode in optoelectronic devices such as organic solar cells, flexible OLED displays, and in touch screen applications [4–6]. In each of these devices the electrode must be transparent and be able to transport electrons away from the active layer. One primary challenge for using Cu in nanoelectronics is its tendency to oxidize in O_2-rich environments; this leads to the formation of an oxide layer comprised of CuO and Cu_2O, which can quickly diminish the conductivity of the metal [7]. In microprocessors, Cu interconnects supply power to the various components in integrated circuits, but are generally embedded below the surface to prevent oxidation [8]. In optoelectronic devices, Cu is attractive because it is abundant and cheaper than ITO [9]. However, both in microprocessors and optoelectronic devices, more flexibility could be achieved if the oxidation of copper could be slowed, or preferably prevented.

The oxidation of Cu can be reduced through passivation [5,8,10]. One approach to Cu passivation is the incorporation of graphitic carbon into the structure of Cu. Graphene on Cu surfaces has been shown to be an impenetrable barrier to oxygen [11]. Graphene [12–14] and CNTs [15–17] have also been considered in nanoelectronics because of their high electrical and thermal conductivities. Incorporating C in the Cu host lattice could improve electrical conductivity of the combined product given the superior performance of graphitic nanostructures, when compared to Cu. Some reported structures are promising but require a sandwich [18], or two-step process [4], where fabrication of the active layer occurs in one step and then transferred to a transparent substrate. This makes commercialization of transparent conducting electrodes using these techniques challenging, so different approaches are still being investigated.

Until recently [19], attempts to combine C with Cu have been quite limited due to the low solubility of C in Cu [20]. In our previous work, we demonstrated transparent conducting films made from Cu covetic, but with low C concentration (<0.1 at.%) [21]. In order to investigate the effect of higher C content we deposited

* Corresponding author.
E-mail address: riba@umd.edu (L.G. Salamanca-Riba).

http://dx.doi.org/10.1016/j.carbon.2017.06.047
0008-6223/

Table 1
Deposition conditions used for Cu cv 4% films using PLD.

Film Conditions	Laser Power (W)	Substrate Temp (C)	Deposition Time (mins)	Film Thickness (nm)	C concentration from XPS[a] (at.%)/(wt.%)
1	1.93	150	15	10	no C
2	3.55	150	20	11	no C
3	3.2	150	60	13	seg. C
4	2.4	150	60	10	2.62/0.44
5	3.3	350	64	20	no C
6	2.6	500	60	21	5.20/1.1
7	2.0	500	120	27	19.14/4.1

[a] Based on carbon and copper only, oxygen excluded from calculation.

copper covetic films using pulsed laser deposition (PLD). PLD is known to transfer ions, molecules and larger structures in the ablation process. As such, we sought to employ this method to transfer graphitic structures embedded in the Cu lattice of a bulk Cu covetic target into thin films. Using PLD we were able to transfer Cu and C simultaneously in a one step process onto a substrate. Films were deposited on Si (100), and sapphire (α-Al_2O_3) ($11\bar{2}0$) substrates using a Cu covetic target with a nominal C concentration of 4 wt% (denoted Cu cv 4%). The laser power, substrate temperature and deposition time were tuned to achieve a conducting, optically transparent film. In this paper we present a detailed analysis of the synthesis, characterization and properties of Cu cv 4% films made by PLD and report that graphitic carbon is uniformly dispersed in a polycrystalline Cu film. Furthermore, these films show reduced oxidation and improved electrical stability over time.

2. Results and discussion

PLD of copper, under similar conditions as described here, has been previously studied in great detail [22]. In order to produce a transparent conducting film from the copper covetic bulk, the optimum photoablation parameters must be ascertained to ensure that the carbon structures are transferred from the target to the film. The substrate temperature and laser power also influence the structure and properties of the film. Cu covetic is comprised of Cu and C, where each element has a different interaction with the laser beam and can give rise to preferential sputtering of one element over the other. In order to produce a homogeneous film, the deposition parameters were altered and the resulting structure of the films analyzed. Spectroscopy techniques such as x-ray diffraction (XRD), x-ray photoelectron spectroscopy (XPS), energy dispersive x-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS) as well as microscopy techniques such as atomic force microscopy (AFM), conductive AFM (C-AFM), and transmission electron microscopy (TEM) were used to characterize the PLD films. 4 point-probe and UV-VIS spectroscopy were used to investigate the electrical and optical properties, respectively. Table 1 presents a sample of the PLD films in this study with corresponding photoablation parameters. All films were grown in 100 mTorr of 99.999% Argon. PLD films (1–6) were grown on Si(100) substrates, while film (7) was simultaneously deposited on Si(111) and Sapphire (α-Al_2O_3). Films of pure copper were also grown by PLD under the same conditions for comparison.

In our previous work, we showed that a 30 nm thick Cu covetic film made by e-beam deposition exhibited a sheet resistance of 2 Ohm/sq and 28% transmittance at 550 nm [21]. We attempted to improve these optoelectronic properties by increasing the carbon concentration in the deposited films using PLD. Films 1–4 in Table 1 were deposited at a constant temperature of 150 °C in order to optimize the laser power, while films 5–7 demonstrate the effect of temperature. XRD spectra from films (2)–(7) are shown in Fig. 1(a). Films 1, 2, 3 and 5, produced with laser powers >3 W or <2 W are not uniformly metallic films. At these laser powers Cu was preferentially sputtered from the target, and was soon oxidized to Cu_2O. In films = 3, C is sputtered first, but is segregated from the Cu layer. Film 4, while homogeneous in composition (by XPS), was mostly amorphous (by selected area electron diffraction in TEM) and along with film (5), which was completely amorphous, exhibited high electrical resistivity (20 M Ohms). In contrast, film (6) deposited on Si (100) and film (7) deposited simultaneously on Si (111) and sapphire were both fabricated at laser powers between 2 and 3 W and at high temperature (500 °C). Both films show strong Bragg peaks at $2\theta = 44$ and 52° corresponding to Cu (111) and (200) reflections, respectively, without evidence of any oxide phases. They demonstrate that we were able to produce homogeneous crystalline films with uniform carbon content throughout the film thickness and independent of the substrate material. Films 2, 4 and 5 do not have significant Bragg peaks. However, for the polycrystalline films we can calculate the grain size listed in Table 2 from the Cu (111) and Cu (200) peaks using the Scherrer equation: $\tau = k\lambda/\beta\cos(\theta)$, where, τ is the mean grain size, k is a dimensionless shape factor with a typical value of about 0.9, λ is the X-ray wavelength, β is the FWHM of the peak and θ is the Bragg angle (in degrees).

XPS depth profile from film (7) on Si substrate, shown in Fig. 1(b), measured an average C content of 4.1 wt% (19.14 at.%) in

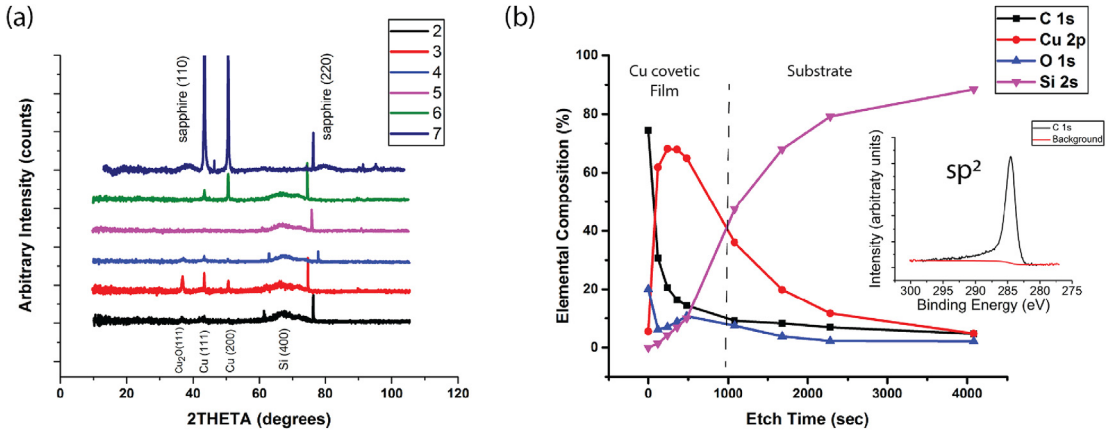

Fig. 1. (a) X-ray diffraction of the Cu cv 4% films grown via PLD described in Table 1, (b) XPS of film (7) on Si(111) substrate showing an average of 4.1 wt% (19.14 at.%) C concentration in the film region, with the inset showing the C 1s peak after 240 s of sputtering.