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B. Balamurugan, B. R. Mehta, and S. M. Shivaprasad

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## "Nanoparticle route" for the synthesis of a stable and stoichiometric $Cu_2C_2$ phase—a semiconductor material

B. Balamurugan and B. R. Mehta<sup>a)</sup>

Thin Film Laboratory, Department of Physics, Indian Institute of Technology Delhi, New Delhi-110 016, India

S. M. Shivaprasad

Surface Physics Group, National Physical Laboratory, New Delhi-110 012, India

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A stable and stoichiometric  $Cu_2C_2$  phase in nanoparticle form has been synthesized using activated reactive evaporation technique. X-ray diffraction, transmission electron microscopy, and x-ray photoelectron spectroscopy studies reveal the formation of a stoichiometric  $Cu_2C_2$  nanophase having a tetragonal structure.  $Cu_2C_2$  samples have a high absorption coefficient with a size-dependent optical absorption edge and *n*-type semiconducting nature. Due to its structural stability, chemical compatibility with other low-cost semiconductor materials, and suitable electrical and optical properties, the  $Cu_2C_2$  phase has the potential of emerging as a semiconductor material. © 2003 American Institute of Physics. [DOI: 10.1063/1.1533852]

In recent years, many metastable and nonequilibrium phases have been successfully synthesized using the "nanoparticle route." The ability to stabilize nonthermodynamical phases by synthesizing them in nanoparticle form has been explained due to the influence of stresses, modifications due to surface structure, large concentration of defects, alterations in Gibbs free energy, and changes in bonding configuration at small sizes.<sup>1–7</sup> A number of nanophase materials also exhibit better postdeposition stability in comparison with the bulk and polycrystalline materials.<sup>8</sup> In addition, the quantum confinement and enhanced surface effects at nanodimensions make the nanoparticle route an excellent methodology to tune optical and electronic properties.<sup>9,10</sup> Optical absorption edge, absorption coefficient, conductivity type, conductivity, mobility, and carrier concentrations can be tailored by varying nanoparticle size.

Various copper compounds such as copper oxides, nitrides, and sulphides have been studied extensively due to their excellent optical and electronic properties.<sup>11-14</sup> In comparison, there are only a few reports on copper carbides. Copper carbide is an unusual material having two known phases: dicopper acetylide (Cu<sub>2</sub>C<sub>2</sub>) and dicopper diacetylide (Cu<sub>2</sub>C<sub>4</sub>).<sup>15</sup> The electronic and Fourier transform infrared spectroscopic studies on  $Cu_2C_2$  have shown its polymeric and semiconducting nature.<sup>16</sup>  $Cu_2C_2$  powder in the form of cuprous acetylide polynuclear complexes has been prepared using organometallic synthesis.<sup>17</sup> Cu<sub>2</sub>C<sub>2</sub> layers have been deposited by electrochemical deposition onto copper electrodes.<sup>18</sup> Cu<sub>n</sub>C<sub>2m</sub> (n = 1-15 and m = 1,2) clusters have also been formed by gas phase aggregation.<sup>19</sup> It has been observed in previous studies that the freshly prepared  $Cu_2C_2$ in bulk and polycrystalline forms is shock sensitive and converts to Cu<sub>2</sub>C<sub>4</sub> with a bright explosion.<sup>15</sup> In comparison with  $Cu_2C_4$ ,  $Cu_2C_2$  seems to be an attractive material for optoelectronic devices as the preliminary studies predict Cu<sub>2</sub>C<sub>2</sub>

to have good photoluminescence with a band gap of 1.5 eV and high optical absorbing nature.<sup>16,17</sup> Despite its useful properties,  $Cu_2C_2$  phase has not attracted much attention due to its metastable nature and poor postdeposition stability.

In the present study, the nanoparticle route has been applied to synthesize a stable and stoichiometric  $Cu_2C_2$  phase in nanoparticle film form using an activated reactive evaporation (ARE) technique.<sup>20</sup> Prior to deposition, the chamber having a base pressure of  $5 \times 10^{-6}$  Torr was filled with a mixture of methane and argon  $(CH_4 + Ar)$  gases up to 1 Torr followed by evacuation to  $5 \times 10^{-6}$  Torr. This process was repeated several times to eliminate the oxygen residual species in the chamber for minimizing the possibility of copper oxide formation. The evaporation of high-purity copper through  $CH_4 + Ar$  plasma leads to copper carbide growth. High flow rate (FR) of  $CH_4$  and Ar, high gas pressure (P), and low substrate temperature  $(T_s)$  resulted in the formation of copper carbide nanoparticles on glass and indium doped tin oxide (ITO) substrates. Copper carbide nanoparticle film sample CC1, prepared at  $P = 5 \times 10^{-3}$  Torr, FR=20 sccm, and  $T_s = 30 \,^{\circ}\text{C}$ , and sample CC2, prepared at P = 5 $\times 10^{-3}$  Torr, FR=20 sccm, and  $T_s = 200$  °C have been investigated. A glancing angle x-ray diffractometer (XRD) (Geigerflex-D/max-RB-RU200, Rigaku), transmission electron microscope [(TEM), JEOL TEM 200 CX], x-ray photoelectron spectrometer (XPS) (Perkin Elmer-1257 using a Mg  $K\alpha$  radiation of E = 1253.6 eV and a hemispherical section analyzer with 25 meV resolution), and optical spectrophotometer (Hitachi-330 UV-VIS-NIR) have been used to characterize the copper carbide nanophase. A Keithley 224 programmable current source and Keithley 2182 nanovoltmeter have been employed for the electrical measurements using van der Pauw's configuration. Schottky junctions were formed by vacuum evaporation of silver (Ag) onto the Cu<sub>2</sub>C<sub>2</sub> nanoparticle films deposited on ITO substrates.

The x-ray diffractogram of the nanoparticle film sample prepared at  $30 \,^{\circ}$ C (sample CC1) is shown in Fig. 1. The crystal structure of the copper carbide lattice has been deter-

a)Author to whom correspondence should be addressed; electronic mail: brmehta@physics.iitd.ernet.in



FIG. 1. X-ray diffractogram of copper carbide nanoparticle film sample CC1. TEM micrograph (inset) of sample CC1 clearly shows the nanoparticle nature.

mined from the observed "d" values by using an analytical method.<sup>21</sup> This analysis shows that the copper carbide nanoparticles have tetragonal crystal structure with lattice constants: a=4.94 Å and c=5.23 Å. The observed d and the corresponding calculated (*hkl*) values are 2.93 Å, (111); 2.47 Å, (200); 2.09 Å, (112); 1.81 Å, (202); 1.55 Å, (310); 1.50Å, (311); 1.45 Å, (222); and 1.27 Å, (400). The broad peak at about  $2\theta=25^{\circ}$  corresponds to the glass substrate. Some low-intensity peaks could not be identified. The values of the particle size estimated using Scherer's equation for samples CC1 and CC2 are 5.5 and 8.5 nm, respectively. The TEM micrograph (inset of Fig. 1) shows that most of the nanoparticles are in the size range 5–8 nm in sample CC1.

The XPS spectrum of the as-deposited samples has a small oxygen peak due to adsorbed oxygen, which completely disappears on a short Ar ion sputter cleaning. The C 1s and Cu  $2p_{3/2}$  core level XPS spectra of sample CC1 after 5 min sputtering (Fig. 2) seems to be comprised of two peaks, indicating two different copper carbide (probably,  $Cu_2C_2$  and  $Cu_2C_4$ ) phases. Both peaks, C 1s and Cu  $2p_{3/2}$ , have been deconvoluted into two peaks at 285.3 eV (peak A1), 288.2 eV (peak A2) and 933.1 eV (peak B1), 935.7 eV (peak B2), respectively. The absence of the satellite peaks in Cu  $2p_{3/2}$  spectra (which is a strong signature of the CuO phase) and the complete disappearance of the adsorbed oxygen peak upon sputter cleaning rules out the presence of any oxide phase (CuO or  $Cu_2O$ ). The difference in the binding energy of the C 1s and Cu  $2p_{3/2}$  peaks (position of A1, A2 and B1, B2 peaks) from the value of elemental carbon (284.6 eV) and copper (932.2 eV), respectively, confirms the copper-carbon bond formation. In  $Cu_2C_4$  (Cu-C=C-C  $\equiv$ C—Cu), carbon atoms across the triple bond are attached



FIG. 2. Core level C 1s and Cu  $2p_{3/2}$  XPS spectra of copper carbide nanoparticle film sample CC1 after 5 min sputtering. Note that the C 1s peak is magnified (×23) compared to the Cu  $2p_{3/2}$  peak.



FIG. 3. Optical absorption coefficient ( $\alpha$ ) as a function of wavelength ( $\lambda$ ) in copper carbide nanoparticle films (a) sample CC1, thickness 150 nm, and (b) sample CC2, thickness 100 nm.

to the atoms having different electron negativity values in comparison to identical coordination of carbon atoms in  $Cu_2C_2$  (Cu—C $\equiv$ C—Cu). Due to this,  $Cu_2C_4$  is more ionic compared to  $Cu_2C_2$ . Thus, the higher-energy C 1s and Cu  $2p_{3/2}$  XPS peaks (A2 and B2) are assigned to the Cu<sub>2</sub>C<sub>4</sub> phase and lower-energy C 1s and Cu  $2p_{3/2}$  peaks (peaks A1 and B1) are assigned to the  $Cu_2C_2$  phase. The stoichiometric ratio x/y in  $Cu_x C_y$  (x/y = 1.01, 0.51) (calculated using the area of A1, B1; A2, B2 peaks and sensitivity factors for Cu and C) are quite close to the stoichiometric values of 1.00 and 0.50 corresponding to  $Cu_2C_2$  and  $Cu_2C_4$  phases, respectively. This, along with the absence of a  $Cu 2p_{3/2}$  peak corresponding to elemental copper (at 932.2 eV) in the XPS spectra, confirms that Cu is present only in the form of copper carbide. The nanoparticle sample CC1 has a predominant  $Cu_2C_2$  phase (88.8 at. %). Thus, the XPS data together with the XRD results confirm the growth of copper carbide nanoparticles with a stable  $Cu_2C_2$  phase.  $Cu_2C_2$  nanoparticles prepared using the ARE technique in the present study have been observed to be quite stable in normal ambient conditions and do not show any shock sensitive nature. Freshly prepared Cu<sub>2</sub>C<sub>2</sub> in bulk powder form is reported to be unstable. A solid-state reaction known as the Glaser oxidative coupling reaction converts bulk Cu<sub>2</sub>C<sub>2</sub> into Cu<sub>2</sub>C<sub>4</sub> phase.<sup>15</sup> The stability of the  $Cu_2C_2$  observed in the present study is a consequence of the nanoparticle nature. As already mentioned, the influence of nanoparticle size on the growth and stability of various crystallographic phases has been studied in various nanoparticle systems such as Cu<sub>2</sub>O, CeO<sub>2</sub>, PbTiO<sub>3</sub>, PbZrO<sub>3</sub>, Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, BaTiO<sub>3</sub>, and ZrO<sub>2</sub>.<sup>4</sup> The additional surface energy term due to the large nanoparticle surface area modifies the Gibbs energy, resulting in the stability of nonthermodynamical phases.<sup>22</sup> The structural defects, lattice distortions, and changes in the bond character at small size have also been observed to enhance the nanophase stability.4-7

The optical absorption coefficient ( $\alpha$ ) of the copper carbide nanoparticle films (Fig. 3) has been evaluated in the wavelength region 0.35–1.5  $\mu$ m from the reflectance, transmittance, and thickness data.<sup>23</sup> A high value of  $\alpha$ ( $\sim 10^5$  cm<sup>-1</sup>) in these samples reveals the strong absorbing nature of the copper carbide. As shown in Fig. 3, strong excitonic peaks are observed at 2.0 eV (sample CC1) and 1.80 eV (sample CC2). The delocalization of the band struc-



FIG. 4. Current–voltage characteristic of  $Cu_2C_2$ –metal (Ag and Al) junctions. Inset shows the device configuration.

ture at nanodimensions results in the predominant excitonic peaks in the optical absorption spectra. The appearance of excitonic features in the absorption spectra of nanoparticles and nanocrystalline films is a signature of the discreteness in the intraband structure due to quantum confinement, and the energy position of the first excitonic peak is normally taken as the absorption edge.<sup>24,25</sup> The band gap of the bulk copper carbide has been reported to be 1.5 eV. The observed blueshift in the optical absorption edge in the copper carbide samples is attributed to the quantum size effect at nanodimensions. The increase in the optical absorption edge from 1.80 to 2.0 eV with decreasing substrate temperature is thus due to the decrease in crystallite size. Hall measurements were carried out on these samples using van der Pauw's configuration. These measurements showed n-type electrical conduction in copper carbide. Electrical conductivity, carrier concentration, and mobility for sample CC1 are 1.3  $\times 10^2~\Omega^{-1}\,\text{cm}^{-1},\,2.4\times 10^{20}~\text{cm}^{-3},\,\text{and}\,3.4~\text{cm}^2/\text{V}\,\text{s},\,\text{respect-}$ tively. The I-V characteristics of the ITO-Cu<sub>2</sub>C<sub>2</sub>-metal (Ag and Al) structures are shown in Fig. 4. The I-V curve of Cu<sub>2</sub>C<sub>2</sub>-Ag shows a good rectifying behavior. The forward bias characteristic is observed on applying negative bias to the  $Cu_2C_2$  layer with respect to Ag contact, and this also confirms its *n*-type semiconducting nature. The linear and symmetric I-V characteristic in the Cu<sub>2</sub>C<sub>2</sub> junction with Al metal indicates that the  $Cu_2C_2$ -ITO (and, also,  $Cu_2C_2$ -Al) contact is Ohmic and the rectifying I-V curve in the case of ITO-Cu<sub>2</sub>C<sub>2</sub>-Ag is due to the Schottky junction formed at the Cu<sub>2</sub>C<sub>2</sub>-Ag contact. The observation of a relatively larger current observed in these devices is due to the nanoparticle nature of the  $Cu_2C_2$  films. A large surface-to-volume ratio at nanodimensions results in a large interfacial area at the junction interface, and this has been observed to result in a higher forward current density in the CdS and PbS nanoparticle film based Schottky and heterojunction devices.<sup>26,27</sup>

The structural, optical, and electronic properties of the  $Cu_2C_2$  phase make it suitable for various applications. Use of  $Cu_2C_2$  in conjunction with other copper compound semiconductors (CuO, Cu<sub>2</sub>O, and Cu<sub>2</sub>S) for hetrojunction solar cells is one such example. In junction devices based on Cu<sub>2</sub>O, CuO, and Cu<sub>2</sub>S, the diffusion of Cu to other noncopper compound semiconductors (CdS, ZnS, ZnSe, CdO, ZnO,  $In_2O_3$ , and  $SnO_2$ ) has been the most nagging problem affecting the stability and efficiency of these devices.<sup>11</sup> Use of  $Cu_2C_2$  in these devices will significantly reduce this problem.

In summary, this is a report on the application of the nanoparticle route for the synthesis of a stable and stoichiometric  $Cu_2C_2$  phase using the ARE technique. The observed stability and preferential growth of  $Cu_2C_2$  is linked to the nanoparticle nature. It has been shown that  $Cu_2C_2$  has a tetragonal unit cell with lattice parameters a=4.94 Å and c= 5.23 Å.  $Cu_2C_2$  nanoparticle films exhibit good electrical conductivity, *n*-type semiconducting nature, high optical absorption coeffecient, and a size-dependent absorption edge. These properties can be fine tuned by controlling the nanoparticle size and postdeposition treatments. The synthesis of a stable nanophase of  $Cu_2C_2$ , shown in the present study, will result in  $Cu_2C_2$  emerging as a semiconductor material for various optical and electronic devices.

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