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Carbon Thin Film Deposition by Electroplating

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Abstract: Carbon thin films were deposited on Aluminum (Al) and Copper (Cu) substrates by electrolysis of methanol. The effect of camphor ($C_{10}H_{16}O$) a natural source, incorporation with methanol is investigated. Camphor with varying amount (1, 2, 3, 4, 5, 7 and 15%) was mixed in methanol solvent to prepare the electrolytes. Aluminum and copper substrates were mounted on the negative electrode. Remarkable change in the variation of current density as a function of applied potential was observed with camphor content. Thin films were deposited on Al and Cu substrates for different percentage of camphor and are compared. Current density is observed to vary with substrate. For both Al and Cu substrates current density was highest for the 2% camphor in methanol solution. The maximum current density with camphor content was different for Al and Cu substrates.

Key words: Carbon, aluminum, copper

INTRODUCTION

There have recently been two important advances in the science of crystalline carbon the discovery that diamond can be readily grown by vapor deposition and the discovery of a third allotrope of carbon, a molecular crystal of the fullcrene molecule, buckyball C_{60}[1]. There has been a parallel advance in effort in disordered carbons. The range of disordered carbons is wide covering soots, chars, carbon fibres, glassy carbon and evaporated amorphous carbon. These carbons are basically sp^2 bonded. A range of new preparation methods has produced forms of amorphous carbon (a-C) and hydrogenated amorphous carbon (a-C: H), which is mechanically hard, infrared transparent and chemically inert. They are finding immediate applications as hard coating materials for magnetic disc drives or as antireflective coatings for infrared windows. Their beneficial properties arise from the sp^3 component of their bonding and these carbons are frequently called diamond like carbon (DLC). In general, such carbons can be fully amorphous or contain crystalline inclusions. This field of non-crystalline carbons is of interest both technologically to materials scientists' and also at a more fundamental level to solid-state chemists and physicists. Precursors and method of deposition of carbon films are the two dominating factors that dictate the optical and electrical properties of the film. And hence these two factors are strongly considered in order to obtain desired carbon thin film having certain optical and electrical properties required for application in various opto-electronic devices. Therefore, researches on finding alternative precursor materials and simple method of deposition have been getting priority all the time. In connection with this research, camphor ($C_{10}H_{16}O$) has been found as an alternative precursor material because it has some advantages[2].

Interest in depositing of carbon thin film has been motivated by properties of this material and the demand of modern technologies, especially those associated with development in the electronic industry. These properties include extreme hardness, chemical inertness, high electrical resistively, high dielectric strength, optical transparency and high thermal conductivity. These properties are tunable from insulating diamond to semi-metallic graphite and therefore, made these films extremely useful in a variety of applications. Deposition techniques that may provide advantages in these applications are of considerable interest. Many studies have been reported on the preparation of carbon thin films. These include chemical vapor deposition[3-4], pulsed laser deposition[2, 5], ion-beam sputtering[6] etc. All the above methods are vapor deposition techniques. However, a deposition of DLC films in the liquid phase is seldom reported. There is experimental evidence that most materials that can be deposited from the vapor phase can also be deposited in the liquid phase using electroplating techniques and vice versa. Enlightened by this conclusion, Namba[7] first attempted to grow diamond phase carbon films in the liquid phase with the aid of an organic solution such as ethanol at a temperature less than 70°C. DLC films had been obtained there, but the choice of a suitable solution

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was limited. Then Suzuki *et al.*[8] made an attempt to deposit carbon films by electrolysis of a water-ethylene glycol solution. Graphite carbon had been obtained according to their result. Nevertheless, ethylene glycol is a viscous solution, which will cause some difficulty in cleaning the substrate after deposition. Hao Wang *et al.,*[9] deposited film by using methanol solution. Methanol is selected because its polarizability and conductivity are stronger than those of ethanol and the structure of methanol is even closer to that of diamond. We have reported semiconducting carbon films by ion beam sputtering[6] and pulsed laser ablation[2,5] obtained from camphor ($C_{10}H_{16}O$), a natural source. In forming carbon films camphor has some advantages over graphite. Graphite is purely sp^3 hybridized whereas camphor consists of both sp^2 and sp^3 hybridized carbon in its structure. Hydrogen in a-C films modifies the properties of the films and introduces many sp^3 sites. Hydrogen passivates the dangling bond in the gap states and also tailors the opto-electronic properties of the film. So while using graphite as the precursor, additional hydrogen gas/ions have to be supplied but camphor has hydrogen abundantly in its structure. Furthermore, the presence of sp^3-hybridized bonds in camphor molecule plays a beneficial role in the deposition of carbon films especially in DLC films. Based on the observations of camphoric carbon films it is suggested that camphor might be suitable candidate as starting materials for semi conducting carbon films in electronic applications.

In the present study carbon thin film deposition was attempted by the electroplating technique using methanol (CH_3OH), as electrolyte. From our earlier experience with camphor as a starting precursor for the preparation of semiconducting carbon films[2,5,6,10,11] we have mixed camphor with methanol. Camphor ($C_{10}H_{16}O$) is a natural source, abundantly available in Asian countries like Japan, China and India. Varying amount (1,2, 3, 4, 5, 7 and 15%) of camphor was mixed to prepare camphor-methanol solution. Aluminum (Al) and copper (Cu) substrates were used for the deposition. Some characteristics of the methanol and camphor-methanol electrolytes are investigated. The effect of substrate used is also studied.

MATERIALS AND METHOD

For the deposition of carbon films on different substrates, an experimental set up is arranged. A schematic diagram of the system is shown in (Fig.1) Copper or aluminum with a size of 3.2x1.5x0.1 cm^3, have mounted on the negative electrode. Prior to deposition the substrates were cleaned in electronic grade acetone (CH_3COCH_3) and methanol (CH_3OH) for 5 minuets at 55°C

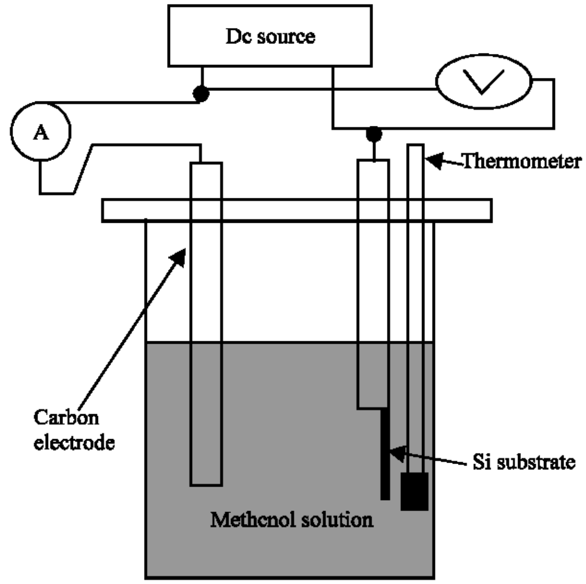

Fig.1: Schematic diagram of the deposition system

successively. The distance between the substrate and positive electrode was set to 1.25 cm. The potential applied to the substrate could be changed from 0 V to 2500 V. A thermometer was adjusted to the system to measure the temperature of solution during the deposition. The P^H measurements were done for different electrolytes before and after deposition. The surface morphology of the deposited films was examined by Scanning Electron Microscopy (SEM).

RESULTS AND DISCUSSION

The substrate current and the P^H play an important role in film formation from an organic solution. Higher current density indicates more polarized charge particles move from solution to electrode, which may have some effect on the growth rate of film. The role of camphor on deposition rate can be understood from the curve of P^H as a function of camphor in methanol (Fig.2). P^H of the solution increases with increasing the percentage of camphor in methanol. The P^H of the methanol containing 1% camphor is about 8. The P^H has increased with camphor content and for the methanol containing 20% camphor the P^H is 8.63. The variation of P^H with camphor content indicates the influence of camphor on deposition rate. The optimum amount of camphor in methanol solution was measured for Al and Cu respectively for maximum current density. The experiment was done for 1, 2,3, 4,5,7 and 15% of camphor. For both substrates, change in current density for different % of camphor was analyzed. Current density was measured for various

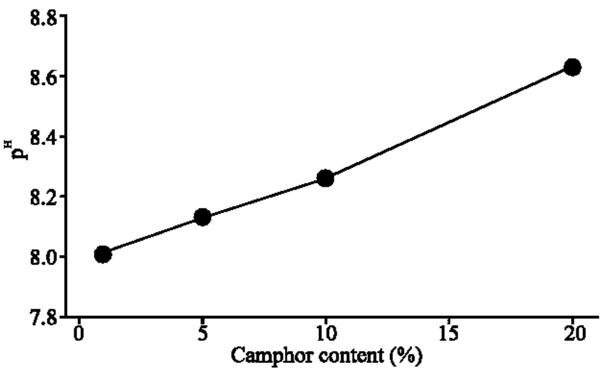

Fig.2: pH as a function of camphor in methanol

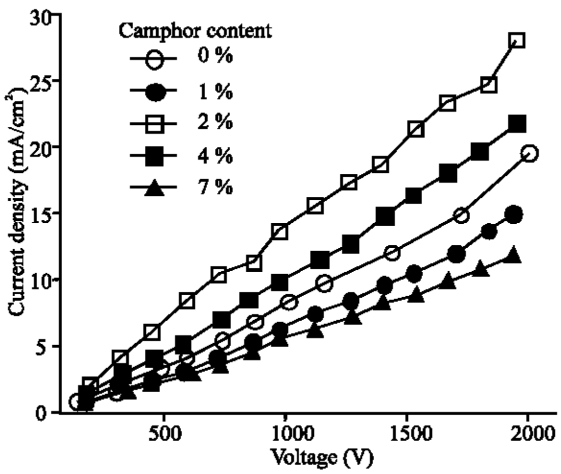

Fig. 3: Current density as a function of applied voltage for different percentages of camphor on Al substrate

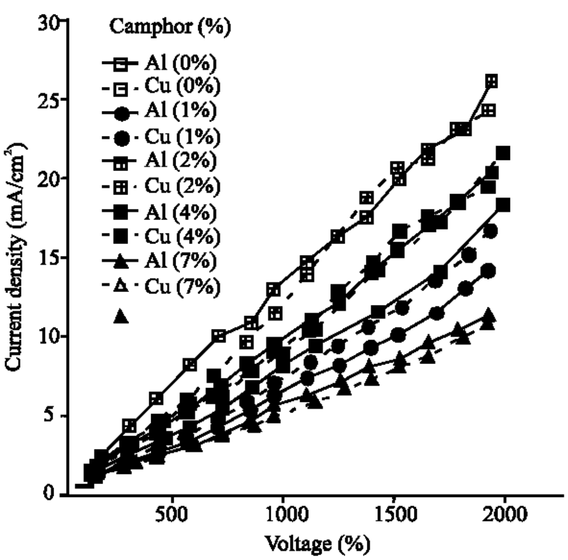

Fig. 4: Current density as a function of voltage for different percentages of camphor on Al and Cu

applied voltages with respect to different electrolytes (camphor content) for Al and Cu substrates. Current density as a function of applied voltage for different percentage of camphor in methanol solution was compared in (Fig. 3) for aluminum substrate.

For 0% camphor content (only methanol solution) a moderate current density pattern was found. By adding little camphor (1%) in the solution the current density is decreased from that of only methanol solution. With increase of camphor content (2%) the current density increased and reached to a maximum value. For further increase of camphor content, the current density is decreased. For the methanol containing 4% camphor, the current density was in between that of 2% and 0%. For 7% camphor content, the current density decreased further and dropped to a value less than that of 1% camphor and indicated the saturation of camphor into the solution. The current density as a function of applied potential is also measured for Cu substrate. Variation of current density with applied potential for Cu substrate is almost similar to that obtained for Al substrate. The variation of current density with applied potential for Al and Cu substrates is shown in (Fig. 4). The current density is decreased initially with camphor (1%) and increased with camphor for 2% camphor in methanol solution. However, with further incorporation of camphor, the current density is decreased. Though the successive variation pattern of current densities for both Al and Cu are alike, they do not show the same magnitude of current densities for same condition. For simplicity and easy assimilation a current density for applied potential of 1500V for both substrates with camphor solution at room temperature is shown in figure 5. It is found that the current density for Cu substrate is comparatively higher than that of Al substrate, especially for higher potential (1,500 V and higher). The current density is decreased initially with 1% camphor and increased to a peak for the 2% camphoric solution. For 2% of camphor content in methanol solution the current density for Cu substrate was 20.83 mA/cm^2 and that for Al substrate was 19.71 mA/cm^2 at 1500V. However with further incorporation of camphor, the current density decreased gradually and for 4% camphoric solution the current density is 16 mA/cm^2 for Cu substrate and 15.3 mA/cm^2 for Al substrate. The current density decreased very rapidly with camphor for the 5% camphoric solution for both the substrates and almost saturation of the current density with camphor is observed with more camphor incorporation. The saturated current density is about 7.5 mA/cm^2 for both substrates.

P^H of solution before and after deposition is measured. P^H of same solution is changed with deposition.

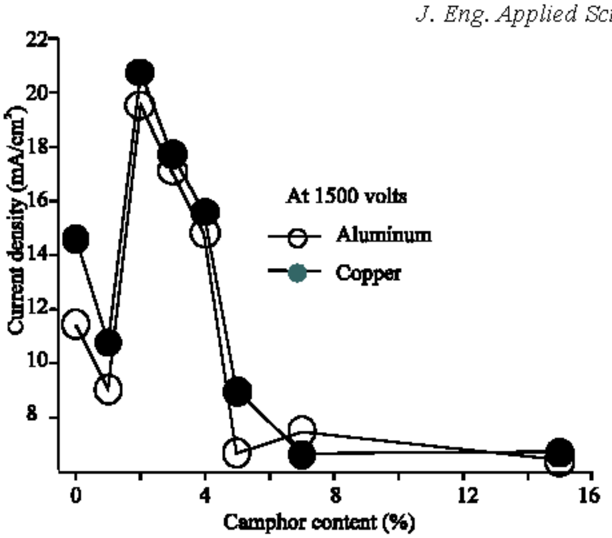

Fig. 5: Current density as a function of % of camphor in methanol at 1500 V for Al and Cu

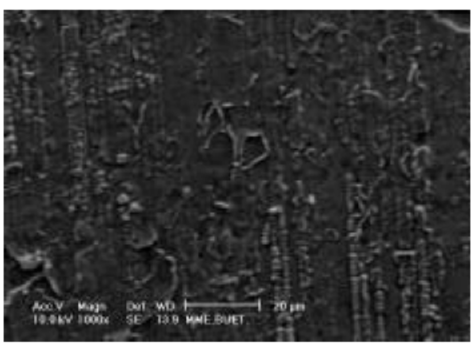

Fig.6: SEM micrograph of the film deposited from 2% camphor in methanol for 8 hrs in Cu

For example during depositing on an Al substrate in a methanol solution with 10% camphor the P^H of the solution was 8.26 before deposition and 7.37 after deposition. The difference in P^H before and after deposition indicates that films are grown from camphor incorporated methanol solution. The surface morphology of the films is observed by Scanning Electron Microscopy (SEM). Figure 6 shows SEM micrograph of a film deposited on Cu substrate (Magnification 1000x) from 2% camphor in methanol solution for 8 hrs. Small grains here show that carbon films are deposited on Cu. Further characterizations of the deposited films are in progress.

CONCLUSIONS

The affinity of copper and aluminum to electro deposition is compared. The role of camphor on electro deposition is also observed. It is found that, for both aluminum and copper substrates the current density decreases initially with camphor from that of only methanol solution and increases thereafter. However, there is a limit for camphor to add in methanol solution for increasing current density. In between two substrates, copper substrate shows higher current density for same conditions. With camphor incorporation in methanol the current density is varied and the deposition rate of the carbon film can be controlled. It is also possible to tune the properties of the carbon film with camphor addition. For application of the carbon films in semiconductor technologies, the usefulness of other substrates such as, silicon is in progress.

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