Pergamon

Materials Research Bulletin, Vol. 34, No. 7, pp. 1173–1178, 1999

0025-5408/99/$–see front matter

PII S0025-5408(99)00108-7

PREPARATION OF CARBON FILMS AT AMBIENT PRESSURE AND TEMPERATURE, USING LASER TRIGGERED PLASMA PULSES

R.D. Saini* and A.K. Dua
Chemistry Division, Bhabha Atomic Research Centre, Trombay, Mumbai 400 085, India

(Communicated by C.N.R. Rao)
(Received July 21, 1998; Accepted August 12, 1998)

ABSTRACT

A novel method is reported for the preparation of carbon films under ambient conditions of pressure and temperature. The substrate is surrounded by a gas mixture containing 10% carbon dioxide in nitrogen. A pulsed carbon dioxide laser is used to trigger the discharge of a capacitor, for producing a pulse of plasma in the gas mixture, and to superficially heat the substrate at the same time. The carbon film has been characterized by scanning electron microscopy (SEM), X-ray photoelectron spectrosopy (XPS), and Raman spectroscopy.

KEYWORDS: A. thin films, B. laser deposition, B. plasma deposition, C. electron microscopy, C. photoelectron spectroscopy

INTRODUCTION

Carbon in its various forms, e.g., amorphous carbon, graphite, diamond, and fullerene, exists in different bonding configurations and is endowed with characteristics varying over a very wide range. Accordingly, there is a large application potential, which is further enhanced when it is in the form of a thin film. Several variants of conventional physical and chemical vapor deposition have been used for the preparation of the films. The former is normally carried out in a vacuum environment, and in the latter, the bulk of the substrate is heated to high temperatures. Laser ablation has also been in vogue for quite sometime now [1]. The recent chance discovery by Pravin Mistry of the use of multiple lasers for diamond deposition under ambient conditions has resulted in a technological breakthrough [2]. This motivated us

*To whom correspondence should be addressed.

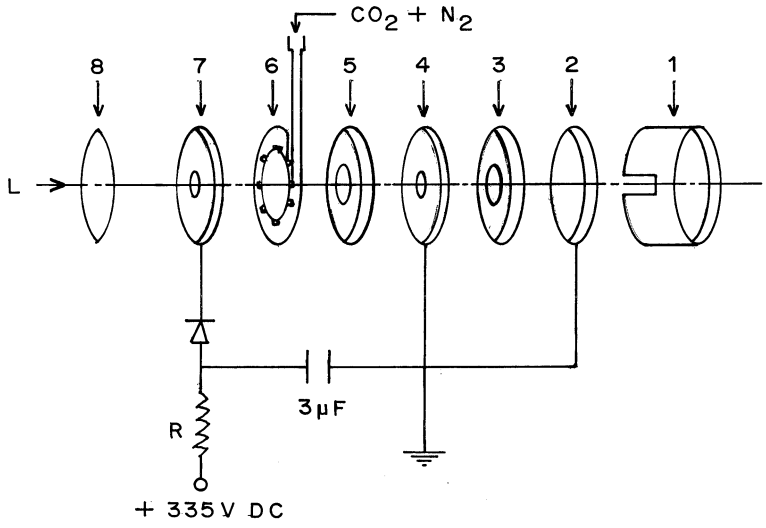

FIG. 1
Schematic of experimental setup (exploded view) for laser-triggered pulse generation: 1 = nylon chamber; 2 = substrate; 3 and 5 = polyethylene rings; 4 and 7 = electrodes; 6 = gas delivery system; 8 = germanium lens; L = CO_2 laser.

to try an alternative idea. In this communication, we report a novel method for the deposition of carbon films by laser triggered discharge of a capacitor in a shroud of a gas mixture of carbon dioxide and nitrogen, surrounding the substrate, under ambient conditions of pressure and temperature.

EXPERIMENTAL

The schematic diagram of the experimental setup is shown in Figure 1. It consists of the following four basic parts: (1) pulsed carbon dioxide laser with focusing optics; (2) suitable chamber for holding (a) the substrate, (b) a gas delivery system for forming a shroud of gas mixture around the substrate, and (c) the electrodes for the generation of the plasma discharge pulses; (3) capacitor and electronics for charging it; and (4) a gas metering and control system for making gas mixtures of predetermined compositions. The laser (Lambda Physik EMG 201) is a grating tuned pulsed TEA carbon dioxide laser operated on the 9R(24) line (1081.1 cm^{-1}). It gives a rectangular-shaped, 25 mm × 15 mm beam with an energy of 600 mJ per pulse and a pulse width (FWHM) of 100 ns (followed by a tail of about 1 μs). A germanium lens of 10 cm focal length was employed to focus it. The chamber is a small nylon tube having a 23-mm outer diameter (o.d.), 20-mm inner diameter (i.d.), 20-mm length, and one end closed. The electrodes are made from 0.5-mm thick nickel sheet in the form of 20-mm diameter discs with a 5-mm diameter hole at the center. The gas delivery system is made from a stainless steel capillary tube (1.6 mm o.d. × 0.8 mm i.d. × 200 mm length), one end of which is connected to the gas supply line; the other end is blocked and bent in to the shape of a circle of 20 mm o.d. Along the inner circumference of this circularly shaped tubular ring, 10 equidistant fine perforations located in the central plane are made to deliver the gas in the

form of fine jets directed towards the center. The nickel electrodes, the gas delivery system, and the substrate are all packed into the chamber. The gas delivery system is spot-welded to the anode, which is insulated from the cathode with the help of a 3-mm thick polyethylene ring. The cathode, in turn, is separated from the substrate by another 3-mm thick polyethylene ring. This assembly is suitably clamped, and the electrical connections are made as shown in Figure 1.

A gas mixture containing 10% carbon dioxide and 90% nitrogen was used. The gas metering and control were carried out using MKS mass flow controllers. The capacitor (3 μF) is charged to 335 Vdc with a neon lamp connected across it for monitoring its charge and discharge cycles. The laser is operated at a repetition rate of 40 pulses per minute. It is focused through the shroud of the gas onto the substrate to the extent that a dielectric breakdown occurs in the gas mixture, thereby causing the discharge of the capacitor. The role of the CO_2 laser is twofold, namely, triggering of the plasma (capacitor) discharge and pulse heating of the substrate, both synchronized to each other. The substrate used was a 1-mm thick, 20-mm diameter disc of molybdenum. It was metallographically polished, ultrasonically cleaned in acetone, and vapor-degreased in isopropyl alcohol.

The capacitance of the capacitor and the composition of the gas mixture were optimized based on the following observations: (1) larger capacitance produced a higher energy plasma discharge, thereby causing significant sputtering of the electrodes/other construction materials, ablation of the substrate and leading to the formation of deep pits and spurious deposits on it; and (2) 100% carbon dioxide gave rise to a very small amount of black-colored deposit on the substrate. Thermodynamic calculations showed that the combined energy available from the laser and the capacitor discharge was too little to decompose the amount of carbon dioxide with which it was interacting; the excess carbon dioxide was, perhaps, quenching the reactive intermediates. The hole size of 5 mm diameter in the electrodes was also optimized by experiments.

About 13,000 pulses were used in the present experiments. The deposited film was stored in an ambient environment before being characterized by scanning electron microscopy (JEOL JSM 330A) for morphology and by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy for composition. Before the XPS measurements, the sample was sputter-cleaned. It was then excited by Mg Kα radiation under 1.33×10^{-7} Pa vacuum using a Riber XPS system comprised of an X-ray source (model CX 700) and an electron energy analyzer (model MAC2). The data were collected and analyzed using a PC-compatible system. The binding energies were referenced using a Au-$4f_{7/2}$ peak. Raman measurements were carried out in backscattering geometry, using the 514.5 nm line of Ar^+ laser at a power of 200 mW.

RESULTS AND DISCUSSION

The deposit was grayish-white in appearance and covered an area of about 2.5 mm × 2.5 mm, equal to the size of the laser spot falling on the substrate. Optical microscope examination showed the deposit to consist of an almost transparent and colorless particulate material. Some particles dispersed the illuminating light into several colorful reflections. SEM examination of the film revealed the particulate structure (Fig. 2), the particulate size being roughly 0.5–2 μm. The crystallites had a rounded polygonal shape, and the film was semicontinuous and multilayered.

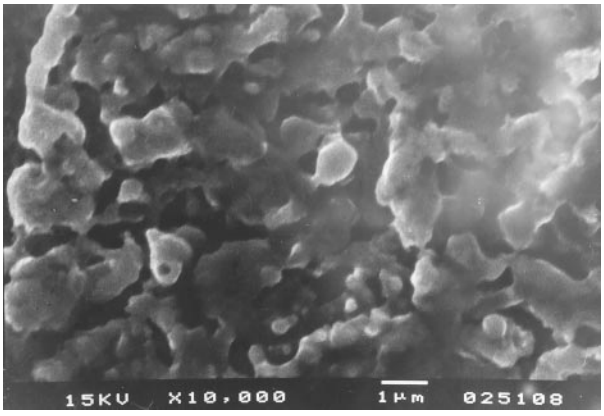

FIG. 2
SEM picture depicting the morphology of the film.

A survey profile of the X-ray photoelectron spectrum of the deposit is shown in Figure 3. There are four peaks corresponding to O (1s), Mo (3p), C (1s), and Mo (3d), besides the Auger peak of O (KLL). Obviously, the molybdenum signal originated from the substrate, because (1) the area covered by X-ray beam is larger (about 10 mm dia.) than what is occupied by the deposit on the substrate and (2) the deposit itself is not fully continuous.

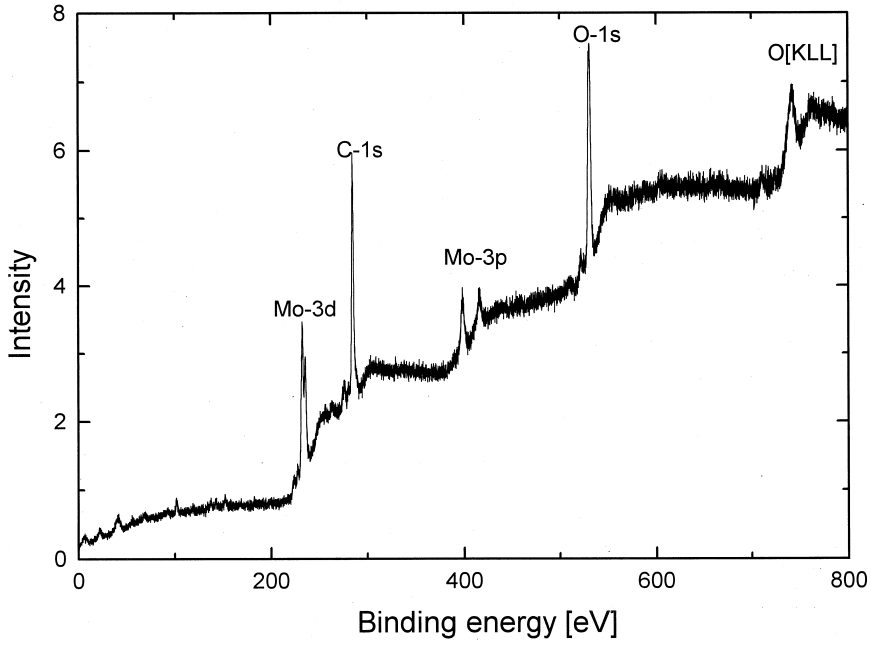

FIG. 3
XPS survey spectrum of the film.

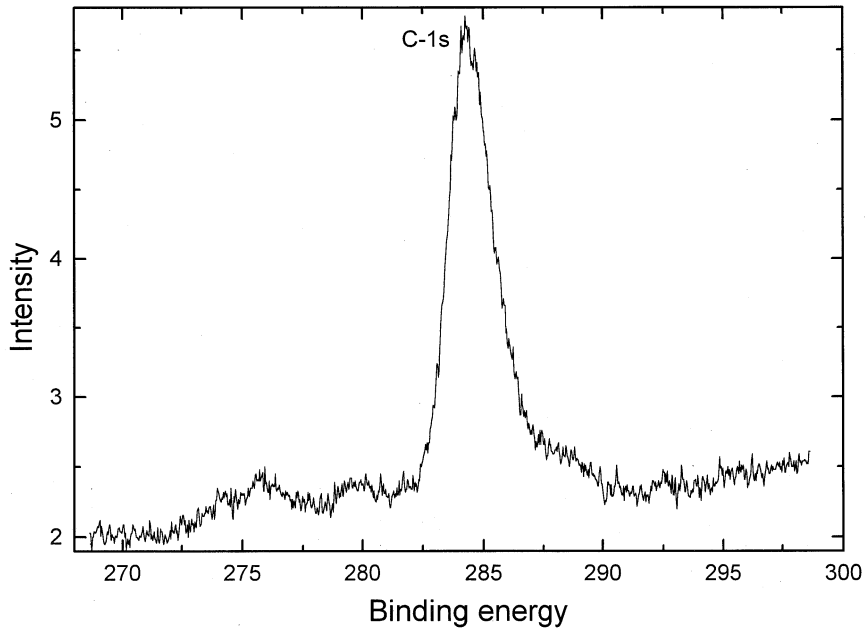

FIG. 4
Expanded XPS spectrum of the film.

Evaluation of the binding energies from the high-resolution molybdenum and oxygen peak positions points to the compound being MoO_3. This is not surprising in view of the fact that molybdenum is easily oxidized in an atmospheric environment. Thus, the deposit consisted primarily of carbon. The expanded XPS spectrum in Figure 4 shows the peak at 284.7 eV, compared with the value of 284.3 eV for C (1s) in C–C bonding [3]. The slight shift of 0.4 eV to higher binding energy is indistinguishable within our resolution.

The Raman spectrum of the sample did not give pronounced peaks with a large signal-to-noise ratio, but indicated the presence of graphite (1580 cm^{-1}), glassy carbon (1343 and 1591 cm^{-1}), and nanocrystalline diamond (1150 cm^{-1}) [4]. Nevertheless, the customary 1332 cm^{-1} peak, the fingerprint signature of cubic diamond, could not be ascertained unambiguously.

Thus, carbon films consisting of different crystallographic forms were deposited on the substrates. By employing more powerful lasers, it may be possible to obtain high deposition rates.

CONCLUSIONS

Carbon deposition by laser-triggered plasma pulses is a novel method. It can be carried out in an environment comprising of ambient pressure and temperature. Another good feature of the method is that only the top slice of the substrate surface is heated, which prevents undesirable effects on its bulk mechanical properties, such as toughness.

ACKNOWLEDGMENTS

The authors are thankful to Dr. J.P. Mittal, Director Chemistry Group, for his keen interest in this work. They also thank Mr. K.P. Muthe and Dr. J.C. Vyas of TPPE Division, BARC, for help in XPS analysis of the thin film samples and Dr. (Mrs.) V. Sugandhi of Spectroscopy Division, BARC, for her help in laser Raman spectroscopy.

REFERENCES

1. A.P. Malshe, S.M. Chaudhari, S.M. Kanetkar, S.B. Ogale, S.V. Rajarshi, and S.T. Kshirsagar, *J. Mater. Sci.* **4/5**, 1238 (1989).
2. P. Mistry, M.C. Turchan, S. Liu, G.O. Granse, T. Baurman, and M.G. Shara, *Innov. Mater. Res.* **1**, 193 (1996).
3. B.R. Stoner, G.H.M. Ma, S.D. Wolter, and J.T. Glass, *Phys. Rev. B* **45**, 11067 (1992).
4. D.S. Knight and W.B. White, *J. Mater. Res.* **4**, 385 (1989).