AMORPHOUS CARBON FILMS

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Abstract

Hydrogenated amorphous carbon (a-C:H) films possessing diamond-like properties are surveyed and discussed with respect to deposition techniques, film characteristics and proposed applications. Recent trend to further modify these films by inclusion of metals into the carbon matrices are summarized and illustrated by our latest results on a-C:H structures containing gold, silver or copper clusters.

Introduction

Study of carbonaceous thin films has witnessed remarkable progress, especially within the last ten to fifteen years, and numerous review (1-4) already exist on this subject. In the present paper we present a summary of data on amorphous hydrogenated carbon (a-C:H) structures spread across the literature; in particular, we emphasise some common feature of films deposited under apparently different conditions (first part), and we point out the attractive possibilities to further modify carbonaceous layer by incorporation of metal clusters (second part) (5).

General considerations

The interest in carbonaceous deposits of unusual characteristics appeared to arise in two steps. The first one started in the fifties with the announcement of carbon layers possessing "diamond-like properties by Schmellenmeier in 1955 (6), followed by further works on films grown on ion or electron irradiated surfaces and investigated for their electrical behaviour (e.g.7): More intensive studies on a-C:H films have been appearing since the seventies, when the interest in the basic structure as well as potential applications were widely recognized.

In most cases a-C:H films are grown in hydrocarbon (H-C) plasmas under energetic ion bombardment (therefore the nomenclature "i-C films" is sometimes used). As some microscopic characteristics of the deposits are reminiscent of diamond, the description diamond-like carbon (DLC) is often applied. These
films are basically amorphous, contrary to semicrystalline or crystalline diamond structures obtained under rather different conditions (8,9).

Some recent parallel studies on bulk carbon are worth mentioning. It has been widely accepted for a long period of time that carbon exists only in the graphite and diamond phases based on sp² and sp³ hybridations. Nevertheless, a new phase diagram for carbon has been suggested by Whittaker (19) introducing a low pressure-high temperature phase of carbenes (sp¹). They appear predominantly in linear chain configuration (polyene), rather than in crystalline networks. Up to now about 10 linear polymorphs have already been discovered (11). Even if their thermodynamic stability is substantially lower than that of graphite, it seems that carbenes may be "frozen-in" by rapid cooling and then exist metastably under normal conditions.

Growth of a-C:H films

Deposition of a-C:H films is usually performed in plasma systems producing sufficient concentrations of energetic species bombarding the growing organic layers. In most cases the films are prepared from hydrocarbon monomers, often mixed with inert gases, especially argon. Radio frequency (RF) discharges have been used most often (3, 12-14). A simple version of such a system is illustrated in Fig.1. The a-C:H films are grown on the RF powered electrode, which is capacitively coupled to the RF power supply, and where a high negative DC self-bias potential \( V_b \) develops (15, 16). The growing films are exposed to the plasma and they are modified by simultaneous ion bombardment. Optical emission spectroscopy (OES) and mass spectrometry have been successfully used to study relationships between the plasma parameters and film characteristics (17). It has been shown that ions (e.g. \( C_6H_6^+ \) in the case of an RF discharge in \( C_6H_6 \)) are extracted from the plasma glow, are accelerated by the sheath potential, and are responsible for further fragmentation on the surface. The fragments, E.G. \( C_2 \) but especially \( CH \), are independent of the kind of hydrocarbon gas used as feed. The OES measurements are also very useful when controlling the inclusion of other components, such as metals, into a-C:H matrices (18).

Other techniques have also been applied for deposition of a-C:H films, for example DC glows discharges, where a grid is often placed in front of the cathode to supply secondary electrons so as to compensate for positive charging of the deposit (19); sputtering of carbon using unbalanced DC-magnetron (20), or large area microwave plasma deposition (21), laser evaporation of carbon combined with Ar⁺ ion beam bombardment of the condensing layer (23), and film growth from H-C gases introduced directly into a saddle field source (24) have also been reported.

Comparing the published data, deposition parameters applied in RF plasma systems are usually in the following ranges: power 50-300 W, pressure 1-10 Pa, flow rate 1-10 cm³/min(STP) and substrate bias \( V_b \) from -150 to -1000 V. In DC systems the power is