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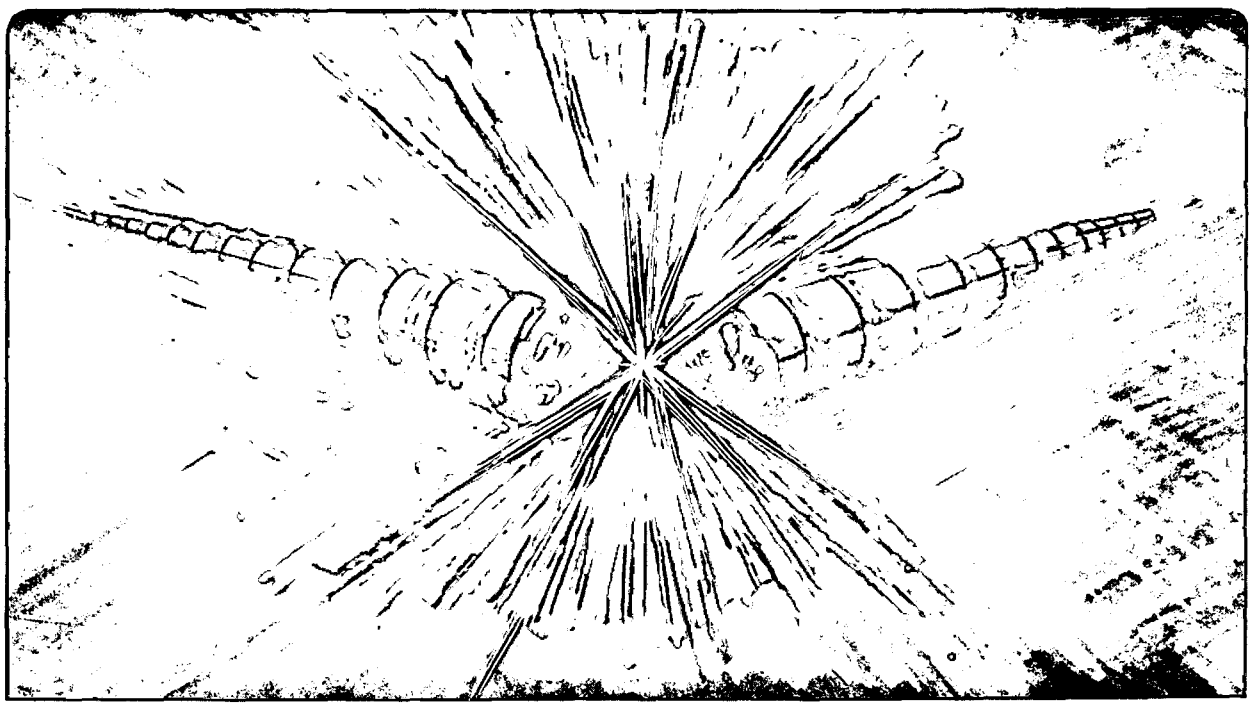

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Simone Anders[1], André Anders[1], C. Singh Bhatia[2], Sébastien Raoux[1],
Dieter Schneider[3], Joel W. Ager III[1], and Ian G. Brown[1]

[1]Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720
[2]SSD/IBM, 5600 Cottle Road, San Jose, CA 95193
[3]Fraunhofer-Institut für Werkstoffphysik und Schichttechnologie,
Helmholtzstr. 20, D-01171 Dresden, Germany

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PROPERTIES OF VACUUM ARC DEPOSITED AMORPHOUS HARD CARBON FILMS

Simone Anders[1], André Anders[1], C. Singh Bhatia[2], Sébastien Raoux[1], Dieter Schneider[3], Joel W. Ager III[1], and Ian G. Brown[1]

[1]Lawrence Berkeley Laboratory, University of California, Berkeley, CA 94720
[2]SSD/IBM, 5600 Cottle Road, San Jose, CA 95193
[3]Fraunhofer-Institut für Werkstoffphysik und Schichttechnologie, Helmholtzstr. 20, D-01171 Dresden, Germany

Key words: Cathodic arc deposition, amorphous hard carbon, elastic modulus, optical gap

Abstract

Amorphous hard carbon films formed by vacuum arc deposition are hydrogen-free, dense, and very hard. The properties of amorphous hard carbon films depend strongly on the energy of the incident ions. A technique which is called Plasma Immersion Ion Implantation can be applied to vacuum arc deposition of amorphous hard carbon films to influence the ion energy. We have studied the influence of the ion energy on the elastic modulus determined by an ultrasonic method, and have measured the optical gap for films with the highest sp^3 content we have obtained so far with this deposition technique. The results show an elastic modulus close to that of diamond, and an optical gap of 2.1 eV which is much greater than for amorphous hard carbon films deposited by other techniques.

1. Introduction

Vacuum arc deposition is an efficient and clean method for forming amorphous hard carbon films [1-4]. If a graphite cathode is used in a vacuum arc plasma source a fully ionized carbon plasma is produced with a kinetic energy of the ions of about 20 eV. When the plasma condenses on a substrate an amorphous hard carbon film is formed. It has been found that the properties of amorphous hard carbon films depend strongly on the energy of the incident ions [1, 4, 5-7]. A technique called Plasma Immersion Ion Implantation can be applied to vacuum arc deposition to tailor the film and interface properties [8, 9]. In this method the substrate is immersed in a plasma (a carbon plasma in this case) and a pulsed negative bias is applied to the substrate. An electric sheath is formed during the bias pulse and ions from the plasma are accelerated toward the substrate. The ion energy is given by the applied voltage and the ion charge state which is one for a cathodic arc produced carbon plasma. During the bias pulses ions are implanted into the substrate whereas between the pulses low-energy deposition takes place. In the early stage of the film deposition intermixing occurs between the substrate and the newly formed film. This leads to excellent interface properties regarding

adhesion. In the later stage of the deposition the film itself is bombarded by the ions which modifies the film. In earlier investigations we have measured film properties such as hardness and elastic modulus [5, 12, 13], mass density [5, 12], coefficient of friction [5], stress [7], Raman spectra [5, 7], sp^3 content [12], and structure [12]. In this paper we describe measurements of the optical properties by ellipsometry and of the elastic modulus using an ultrasonic technique.

2. Deposition

A cathodic arc plasma source with macroparticle filter was used to deposit amorphous hard carbon films on silicon substrates [10, 11]. The graphite cathode of 6 mm diameter was surrounded by a cylindrical anode. The discharge current was 300 A, the duration 5 ms, and the repetition rate 1 Hz. A negative pulsed bias voltage in the range of 0 to - 2000 V was applied to the substrate during immersion in the plasma. The bias pulses had a duration of 2 μs and the pulse off-time was 6 μs. The Si (100) substrates were mounted on a water-cooled holder to keep them at room temperature during the deposition. The base pressure was 10^{-4} Pa.

3. Elastic modulus

The elastic modulus was determined by an ultrasonic surface wave technique [14-16]. In this method surface wave pulses with a broad bandwidth are generated by a nitrogen pulse laser with a wavelength of 337 nm. The ultrasonic signal, which is influenced by the structure of the surface film, was measured by a piezoelectric transducer in the frequency range of 50-250 MHz. The surface wave phase velocity as a function of frequency was determined using a Fourier transform technique. To calculate the elastic modulus of the films the inverse problem of surface wave dispersion in coated materials was solved.
The elastic modulus was measured for a series of amorphous hard carbon films with thickness 100 nm. The films were deposited at various pulsed bias voltages in the range 0 to -2000 V. Fig. 1 shows the elastic modulus as a function of the bias voltage.

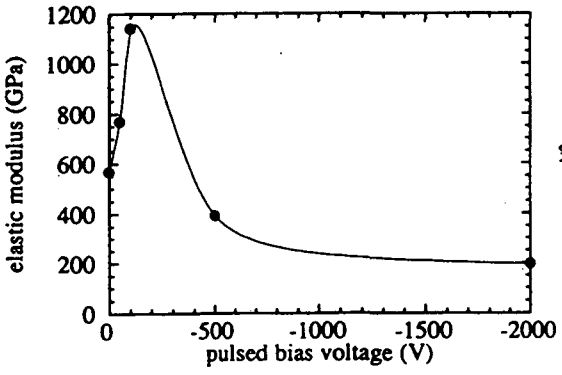

Fig. 1: Elastic modulus of amorphous hard carbon films as a function of the pulsed bias voltage applied during deposition.

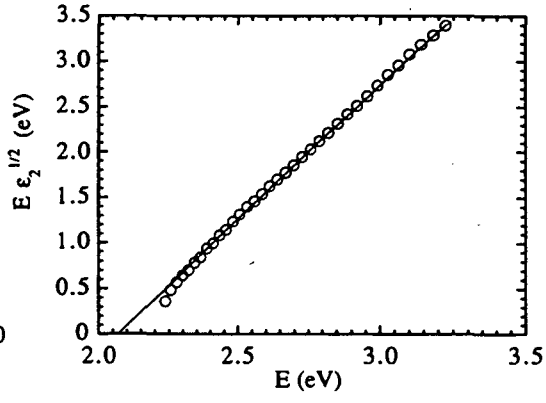

Fig. 2: The optical gap is the intersection with the x-axis of a plot of $E\,\varepsilon_2^{1/2}$ vs. the photon energy E.

4. Ellipsometry

For determining the optical properties of cathodic arc deposited amorphous hard carbon films, we used a spectroscopic ellipsometer. The ellipsometric experimental data $\Psi(h\nu)$ and $\Delta(h\nu)$ have been measured from 1.5 to 4.1 eV for a film deposited at a pulsed bias voltage of -100 V with a thickness of 80 nm on silicon. The measured parameters are defined as $\rho_p/\rho_s = \tan\Psi \exp(i\Delta)$, where ρ_p and ρ_s are the complex reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively. A model assuming three media (ambient/film/substrate) was used to analyze the data with the assumption of film properties interpolating between the properties of graphite and diamond. The best fit of the model to the experimentally determined data was obtained assuming a ratio of 90% diamond to 10% graphite in the film (with an accuracy of ±5%). From the optical constants $n(h\nu)$ and $k(h\nu)$ determined by ellipsometry where n and k are the real refractive index and the extinction coefficient we have calculated the dielectric constants $\varepsilon_1(h\nu)$ and $\varepsilon_2(h\nu)$ using $\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$. The optical gap was determined from

$$E\,\varepsilon_2^{1/2} = B(E - E_0)$$

which is based on the assumption that in amorphous semiconductors the density of states beyond the mobility edge has a square root dependence on energy, and that the centers of the valence and conduction band are parabolic [17, 18]. E is the photon energy, E_0 is the optical gap, and the constant B is proportional to the joint density of states. Fig. 2 shows $E\,\varepsilon_2^{1/2}$ as a function of the photon energy E. Following the analysis method described in [3] the optical gap was determined from this graph to be about about 2.1 eV.

5. Discussion and Conclusions

The elastic modulus determined by the ultrasonic method reaches the highest values for films deposited at - 100 V bias voltage. These results can be compared to the elastic modulus of diamond of about 1140 GPa [14]. This indicates a very high percentage of sp^3 bonds in these films. It has been found that the hardness and the elastic modulus of amorphous hard carbon films are linearly related with a proportionality factor is of order 10 [16]. This also indicates a very high hardness of the films. A comparison to the elastic modulus of these films determined by nanoindentation [12, 13] shows that the data obtained by the ultrasonic method are about a factor of two larger. This might be due to the fact that nanoindentation measures the elastic modulus perpendicular to the films whereas the ultrasonic method determines the elastic modulus parallel to the film.

The optical gap determined by ellipsometry is much larger than for hydrogen-free amorphous hard carbon films deposited by other methods such as laser ablation or sputtering with typical values of 0.5 - 1.5 eV [19]. Only films deposited by cathodic arc deposition have been reported having an optical gap larger than 2 eV [3]. A large optical gap is also an indication of a high sp^3 content (the optical gap of diamond is 5.5 eV).

The maximum of the elastic modulus at - 100 V bias is in agreement with all other measurements we have performed with different methods and for different

parameters, all showing the most "diamond-like" character of the films at this bias voltage.

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LAWRENCE BERKELEY LABORATORY
UNIVERSITY OF CALIFORNIA
TECHNICAL AND ELECTRONIC
INFORMATION DEPARTMENT
BERKELEY, CALIFORNIA 94720