LBNL-41654
Preprint

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Plasma Immersion Ion Implantation and Deposition (PIIID) for the Formation of Hydrogen-Free Diamond-Like Carbon Thin Films

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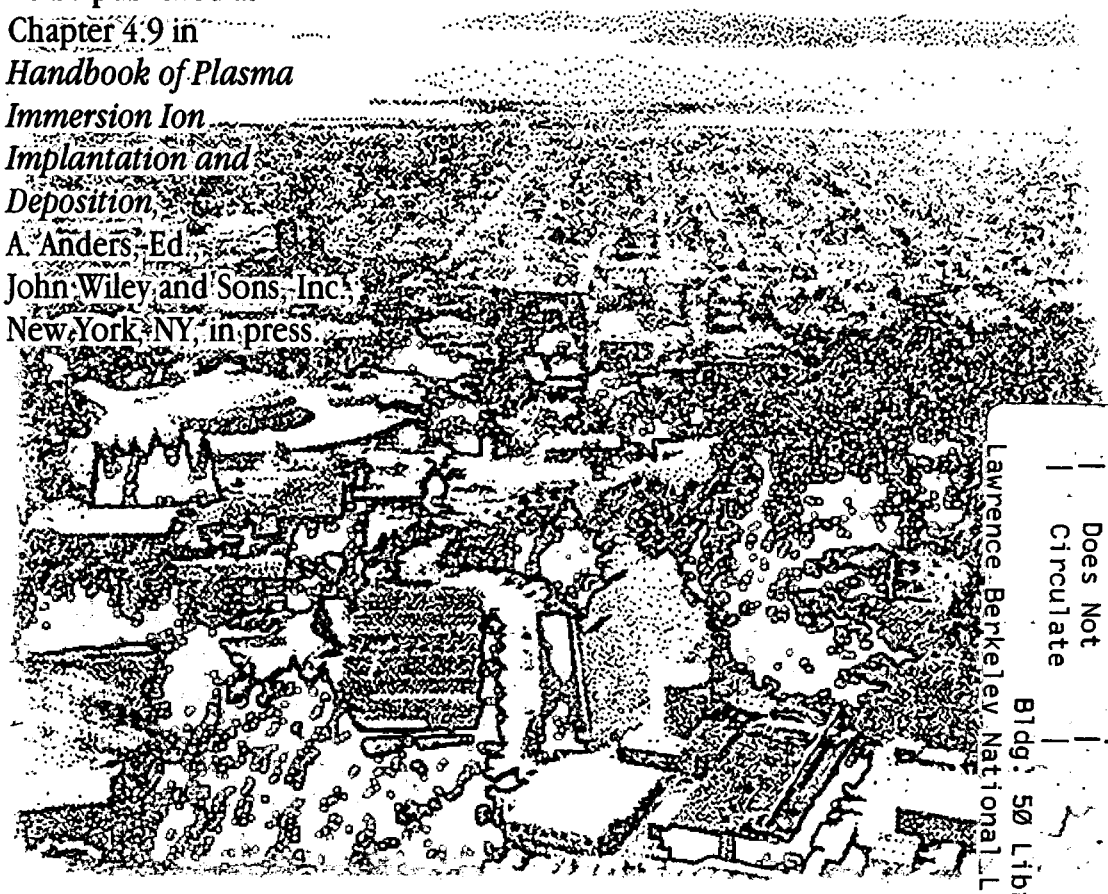
March 1998

To be published as
Chapter 4.9 in
Handbook of Plasma Immersion Ion Implantation and Deposition,
A. Anders, Ed.
John Wiley and Sons, Inc.,
New York, NY, in press



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This work was supported by the Office of Energy Research, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

4.9. Plasma Immersion Ion Implantation and Deposition (PIIID) for the formation of hydrogen-free diamond-like carbon thin films

4.9.1. The nature of hydrogen-free carbon based thin films

Carbon atoms can be bound in various hybridizations, in the sp^1, sp^2, or sp^3 state. The crystalline allotropes of carbon which are diamond, graphite, fullerenes, and nanotubes, show a long range order, whereas in amorphous carbon the atoms are arranged in a three-dimensional network with the absence of order beyond the nearest neighbor. The preferential formation of crystalline vs. amorphous carbon forms depends on the chemical environment in which the film is formed, and strongly also on the carbon ion and atom energy. Polycrystalline diamond can be formed by a number of processes, e.g. chemical vapor deposition, heated filament, plasma torch or flame combustion methods. All these processes usually involve high substrate temperatures and lead to rough films.

This work was supported by the Office of Energy Research, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC03-76SF00098.

Amorphous hard carbon is an alternative material which can contain up to 85% sp^3 bonds which are characteristic for diamond. It can be formed by various methods as well, such as , e.g., sputter deposition (Cuomo et al. 1991b), laser ablation (Cuomo et al. 1991b, Voevodin et al. 1995), mass selected ion beam deposition (Lifshitz et al. 1995, Lifshitz et al. 1997), dual-ion beam deposition (Cuomo et al. 1991a), or filtered cathodic arc deposition (Aksenov and Strel'nitskij 1991, Anders et al. 1994, Fallon et al. 1993, Lossy et al. 1992).

The growth process for pure carbon films (in contrast to hydrogenated films where chemical reactions play a role) can be described by a subplantation and densification model (Lifshitz et al. 1989, McKenzie et al. 1991a). Initially, a very thin (one or two monolayers) film is formed which contains mostly sp^2 bonds which are characteristic for graphite. This layer is subsequently bombarded by carbon ions of a certain energy leading to a penetration of the surface layer by these ions (subplantation). This is causing local compression, stress, densification, and formation of the metastable sp^3 phase. The ion energy necessary for the penetration of the surface layer is about 25eV, but also higher energies up to a few keV can lead to a considerable fraction of sp^3 bonded atoms in the film. An over-constraint system is formed causing high compressive stress in these films. The amount to which the subplantation process forms preferentially sp^3 bonds depends strongly on the carbon ion energy. One way of modifying the ion energy is biasing of the substrate which is particularly efficient with fully ionized plasmas because there is no neutral species and all ions are accelerated by the biasing. Even though similar film properties can be obtained with dc biasing and pulsed biasing of high duty cycle (Anders et al. 1994, Fallon et al. 1993), pulsed substrate bias has two major advantages in comparison to dc bias. First, it is possible to operate at much higher voltages and plasma densities at the substrate (corresponding to high deposition rates) without breakdown between the substrate and the plasma. Second, it is possible (to some degree) to bias substrates with low conductivity which will charge up in the case of dc biasing. This can be important for coatings of insulator materials such as, e.g., plastics or glass in which case the bias voltage is applied to the substrate holder. Cathodic arc deposition using pulsed substrate biasing (PIIID) is very efficient in forming very high sp^3 fraction amorphous

hard carbon films. Therefore we will concentrate in the next section on this deposition method and the use of pulsed substrate bias.

4.9.2. Cathodic arc deposition of amorphous hard carbon film using substrate biasing

It was found already in the seventies (Strel'nitskii et al. 1978) that amorphous hard carbon films grown by cathodic arc deposition show extraordinary properties. It is remarkable that this early work already applied various kinds of substrate bias (dc bias and rf bias of different frequencies) to optimize the film properties. It was observed that the films exhibit a very high hardness and mass density, and that these properties are strong functions of the ion energy (Strel'nitskii et al. 1978, Bakai and Strel'nitskii 1981). Over the last two decades many researchers have extensively studied the properties of these films. We will review the film properties as functions of the applied bias voltage.

Tetrahedral bonding fraction

The fraction of tetrahedral bonds in the diamond-like films is a strong function of the carbon ion energy. It was found by a number of authors (Bakai and Strel'nitskii 1981, Cuomo et al. 1991b, Fallon et al. 1993, Pharr et al 1996, Strel'nitskii et al. 1978) that there is an optimum ion energy to produce the highest tetrahedral fraction for a given deposition process. The sp^3 fraction x is defined as $x=N(sp^3)/(N(sp^2)+N(sp^3))$, where $N(sp^3)$ and $N(sp^2)$ are the numbers of atoms bound in the sp^3 and sp^2 state, respectively. The energy for the highest sp^3 fraction was found to be around 100 eV. Figure 4.9.2.-1 shows the fraction of tetrahedral bonding in cathodic arc deposited diamond-like carbon films as a function of the ion energy. The "natural" ion energy E_0 for a cathodic arc plasma source is about 20 eV for carbon (Aksenov and Strel'nitskij 1991, Chhowalla et al. 1996), therefore the total ion energy is $E_i = E_0 + ZeV$, where Z is the ion charge state (which is 1 for the cathodic arc carbon plasma, Brown et al. 1988), e is the elementary charge, and V the (negative) applied bias voltage. The fraction of tetrahedral bonds is usually

determined by electron energy loss spectroscopy (EELS) (Berger et al. 1988). The sp^3 fraction can reach very high values up to 85% for optimized biasing (Fallon et al. 1993, Pharr et al. 1996).

Mass density

If no voids are present in the films the mass density is directly correlated to the sp^3 fraction of the films. The sp^3 fraction x can be correlated to the mass density of the amorphous carbon film ρ, the mass density of diamond, $\rho_d = 3.5$ g/cm^3, and the mass density of graphite, $\rho_g = 2.0$ g/cm^3 as $x = (\rho_g \rho_d - \rho \rho_d)/(\rho \rho_g - \rho \rho_d)$ (Cuomo et al. 1991b). If the mass density of the film is known, a lower limit (due to the possible existence of voids) of the sp^3 fraction can be estimated from the above relationship. Like all film parameters the mass density is also a strong function of the ion energy. Figure 4.9.2.-2 shows the mass density of cathodic arc deposited diamond-like carbon films as a function of the ion energy. The mass density can be measured by combining Rutherford backscattering spectrometry (RBS), giving the number of carbon atoms per area, and profilometry giving the films thickness (Anders et al. 1994, Fallon et al. 1993). A mass density of 3.0 g/cm^3 was found also by deposition of a thin film on a pre-weighted wafer and weighing the wafer after deposition using -100 V pulsed bias (Bhatia et al. 1998). Also EELS measurements of the mass density as a function of the ion energy are in good agreement with the RBS and profilometry data (Pharr et al. 1996).

Hardness and elastic modulus

Hardness and elastic modulus are typically measured by nanoindentation. This is a measurement which becomes difficult to interpret if the film hardness substantially exceeds the substrate hardness, and if the film is very thin. For thin films (<100 nm and depending on the indentation depth) the values are often more qualitative than quantitative, and great care needs to be taken if one wants to compare results of different groups. Still, these measurements show that cathodic arc deposited carbon films formed at the bias voltage optimized for maximum sp^3 content are very hard and can come close to the hardness of diamond with values up to 95 GPa (Lossy et

al. 1992). High elastic moduli of up to 400 GPa were also measured for films deposited at -100V pulsed bias (Pharr et al. 1996). It is clear from these data that the properties of these films are extraordinary, because the high hardness and elastic modulus are combined with a very high smoothness smaller than 0.1 nm (Salvadori et al. 1998) of the films in contrast to crystalline diamond. Some nanoindentation measurements show a slightly softer surface layer compared to the bulk of the film (Pharr et al. 1996). These findings correlate to transmission electron microscope (TEM) measurements which show a slightly brighter surface layer than the bulk of the film indicating a lower mass density (Pharr et al. 1996, Anders et al. 1998a). This might be a supporting argument for the subplantation model which describes the formation of high sp^3 content films under the surface by very shallow ion implantation. More extreme values for the elastic modulus up to 1100 GPa (Anders et al. 1995a) were found using an ultrasonic surface wave method (Schneider et al. 1992, Schneider et al. 1993, Schultrich et al. 1994). These measurements gave elastic moduli which are about two to three times higher than data obtained by nanoindentation, almost reaching diamond properties. This might be due to the fact that nanoindentation measures the elastic modulus perpendicular to the film whereas the ultrasonic surface wave method measures it along the film.

Compressive stress

Unfortunate for many applications, a high tetrahedral bonding fraction comes along with high compressive stress in the films. Poor adhesion is often a problem caused by high stress. The compressive stress was also found to be a strong function of the ion energy during the deposition. Several authors observed that the stress has a maximum around -100V bias voltage and can reach values up to about 10 GPa (Ager et al. 1995, Fallon et al. 1993, McKenzie et al 1991b). Figure 4.9.2.-3 shows the compressive stress of cathodic arc deposited films as a function of the ion energy determined by measuring the curvature of a thin Si wafer before and after deposition, and applying the Stoney equation for analysis (Windischman et al. 1991). The high stress can influence the Raman spectra as reported by Ager et al. 1995. High stress causes a shift of the

position of the Raman G-band to lower wavenumbers. This was observed by comparing the Raman spectra of adherent and delaminated films. This needs to be taken into account when Raman spectroscopy is used to analyze the film quality, since a lower sp^3 fraction causes a similar shift of the G-band position to lower wavelengths. Films with identical G band position can have very different sp^3 fraction and properties.

Several authors report on attempts to reduce the stress while maintaining the hardness by introducing additional elements in the films (Franceschini et al. 1992, Gangopadhyay et al. 1995). This was successfully done for hydrogenated films of medium hardness around 20 GPa. The incorporation of tungsten into hydrogen-free films for stress reduction was reported by Monteiro et al. 1997. They achieved a considerable reduction of the stress by introducing 0.8 at.% of W by co-deposition from 11 GPa for undoped cathodic-arc deposited carbon films to 4.3 GPa for the W doped films which caused only a small reduction in the hardness from 72 to 63 GPa.

Adhesion

As mentioned before, the high stress has a deteriorating effect on film adhesion. This is an area where pulsed biasing plays an important role and can lead to great improvements. It was found that high pulsed bias can increase the adhesion of films drastically. As demonstrated by TEM measurements and XPS sputter depth profiling (Gerstner et al. 1995), by RBS measurements (Anders et al. 1994), and calculated by computer simulation (Anders et al. 1994, Anders et al. 1998), high bias leads to an intermixing of the film and the substrate. This is a key factor for good adhesion. It was found that the adhesion of well-intermixed films was so good that the adhesion between film and substrate was stronger than the internal strength of the Si substrate (Anders et al. 1995b, Gerstner et al. 1995). If the desired film properties cannot be obtained by high bias, it is often of great benefit for the deposition process to start at high bias for strong intermixing and continue the deposition at the optimum (usually lower) bias for the desired film properties.

Optical properties

The measurement of optical properties is complicated by the fact that in many cases it is necessary for the optical measurements to deposit the film on a transparent substrate which normally cannot be biased. Using ellipsometry and reflectance/transmittance measurements some properties can be determined. It was found that the optical gap for cathodic arc films deposited at -100V pulsed bias is about 2.1 eV (Anders et al. 1995a). Lossy et al. 1992 also measured the optical gap of cathodic arc deposited films and found values between 2.1 and 2.4 eV. McKenzie et al. 1991b measured optical gaps ranging from 2.0 to 3.5 eV for films deposited by filtered cathodic arc deposition. The optical gap was estimated from measuring the optical constants n and k to determine the dielectric function $\varepsilon_1 + i\varepsilon_2$. The Tauc plot is defined as $E\sqrt{\varepsilon_2}$ as a function of E where E is the photon energy. The Tauc plot is used to determine the optical gap by the intercept of the extrapolation of the linear region of the curve with the E axis. It was found that the Tauc plot does not show a very clear linear range for extrapolation leading to a broad range of data for the optical gap. This fact was interpreted as indication of a broad tail on the band edges of a high bandgap semiconductor (McKenzie et al. 1991b).

Electrical resistivity

Cathodic arc deposited carbon films using different substrate bias voltage were used to measure the electrical restitivity as a function of the ion energy (Fallon et al. 1993). It was found that the resistivity varies with the ion energy in the same way as most other parameters, showing the highest value of about 10^9 Ω cm around -100V bias and a decrease to $5x10^5$ Ω cm at -450 V bias. By doping with nitrogen and applying a bias of -20 V the resistivity can be decreased to 1000 to 1 Ω cm (Veerasamy et al. 1995).

Thermal stability

The influence of the substrate temperature on the sp^3 fraction was investigated by Cuomo et al. 1991a for dual-ion beam deposition. It was found that the sp^3 fraction decreases with

increasing substrate temperature. The highest sp^3 fraction of >40% was obtained at 77K whereas the films deposited at 1073K appeared to be basically graphitic.

Thermal stability of cathodic arc deposited films is of concern when the films are applied to tool coatings. The thermal stability was tested in air and in vacuum (Anders et al. 1998b, Anders et al 1998c, McKenzie et al. 1993) and it was found that it is also a function of the applied pulsed bias during the deposition. Figures 4.9.2.-4 and 4.9.2.-5 show the Raman spectra of annealed films deposited at two different pulsed bias voltages of -100V and -2000V (Anders et al. 1998b). The films were annealed for 2 hours in air. The films deposited at a bias voltage of -100V show thermal stability up to 500°C in air, whereas the films deposited at -2000V change their structure starting at 300°C. The films oxidize in air at elevated temperatures. Films deposited at -100V start to show severe oxidation above 500°C whereas films deposited at -2000V start to oxidize strongly at 450°C. In vacuum, films deposited at -100V remain stable up to 700°C. This was found by applying Near Edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy after 30 min. annealing at 10^{-7} Pa (Anders et al 1998c). Similarly, McKenzie at el. 1993 observed a constant plasmon energy for annealing in vacuum of both nitrogen doped and undoped cathodic arc films for temperatures up to 700°C.

Multilayers

The strong dependence of the film properties on the ion energy allows to deposit multilayers of cathodic arc carbon of varying properties. This was tested by applying alternatively low (-100V) and high (-2000V) pulsed bias during a carbon film deposition to deposit carbon/carbon multilayers (Anders et al. 1995c, Anders et al. 1998a). Multilayers were deposited with varying fractions of the low and high bias durations (90%/10%, 50%/50%, and 10%/90%). TEM investigation show the clear multilayer structure for the 50%/50% film (figure 4.9.2.-6). The major effect of multilayer structures is the ability to tailor the film properties through the film and chose certain interface, bulk, and surface properties. In the case of the multilayer structures described above, it was found that the multilayers had a lower stress in comparison to bulk films of

the same hardness. Figure 4.9.2.-7 shows the stress of multilayers in comparison to monolithic films. It was demonstrated that it is possible to some degree to decouple hardness and stress values by using multilayered structures.

Knoblauch et al. 1998 describe the deposition of multilayers consisting of hydrogenated diamond-like carbon by varying the bias voltage for a plasma assisted chemical vapor deposition process. They used the different properties of CH_x as a function of the sample bias to create multilayer structures with soft, graded, and sharp interfaces applying bias voltages of sinusoidal, triangular, and rectangular pulse shape. The multilayers showed a reduced wear in comparison to monolithic films.

All the above mentioned experiments demonstrate that cathodic arc deposited amorphous hard carbon films have properties which make these film excellent candidates for many tribological, wear and protective coating applications. Pulsed substrate biasing is essential for the formation of the highest hardness and sp^3 fraction films in the case of hydrogen free films deposited from a highly ionized plasma.

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Captions for Figures

Figure 4.9.2.-1 Fraction of tetrahedral bonding in cathodic arc deposited diamond-like carbon films as a function of the ion energy.

Figure 4.9.2.-2 Mass density of cathodic arc deposited diamond-like carbon films as a function of the ion energy.

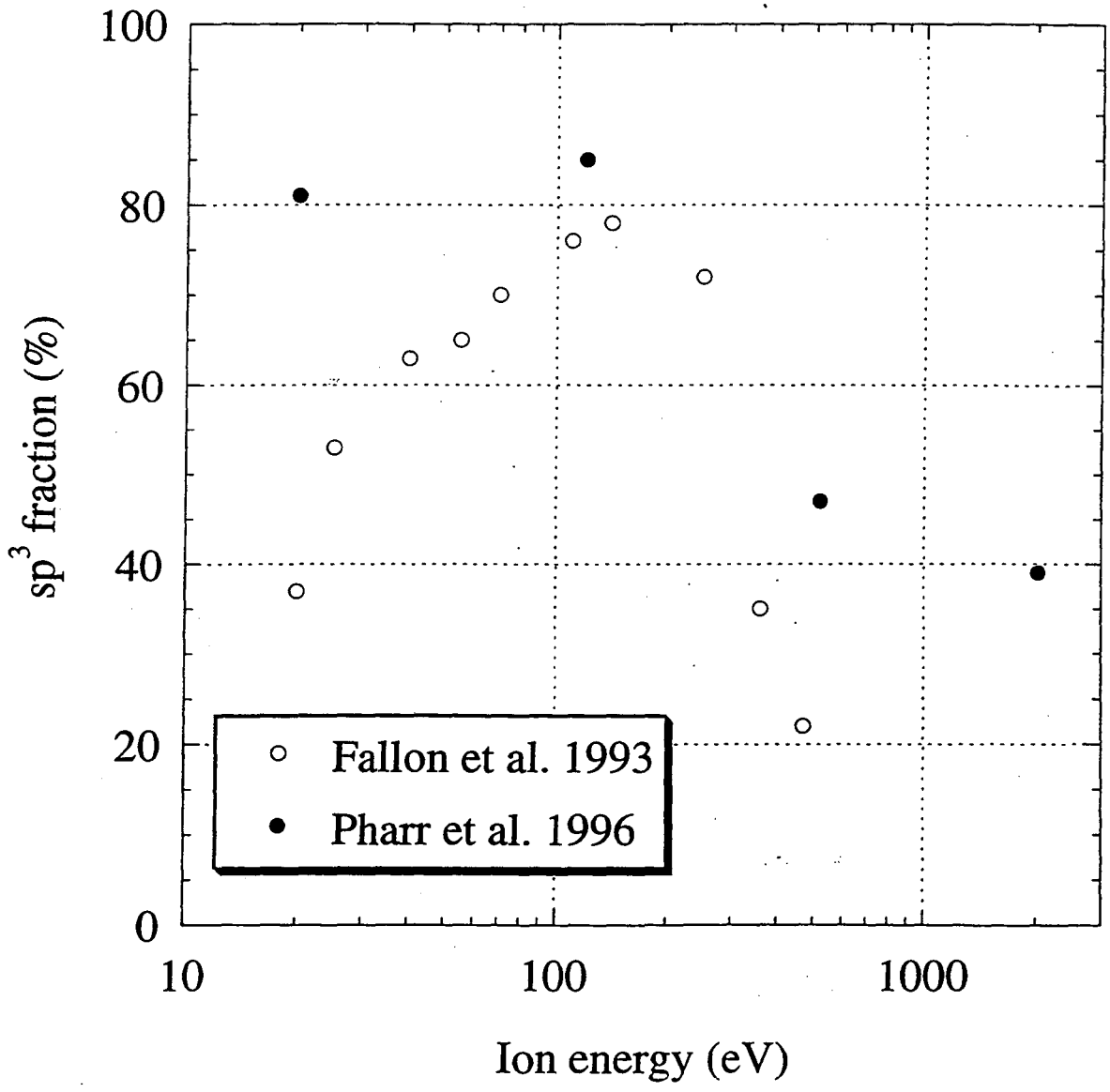
Figure 4.9.2.-3 Compressive stress of cathodic arc deposited amorphous carbon films as a function of the ion energy.

Figure 4.9.2.-4 Raman spectra of cathodic arc carbon films deposited at a pulsed bias voltage of -100V annealed in air for 2 h.

Figure 4.9.2.-5 Raman spectra of cathodic arc carbon films deposited at a pulsed bias voltage of -2000V annealed in air for 2 h.

Figure 4.9.2.-6 TEM image of multilayer structure for cathodic arc carbon films deposited alternatively with high (-2000V) and low (-100V) pulsed bias voltage.

Figure 4.9.2.-7 Compressive stress of cathodic arc deposited multilayers in comparison to monolithic films.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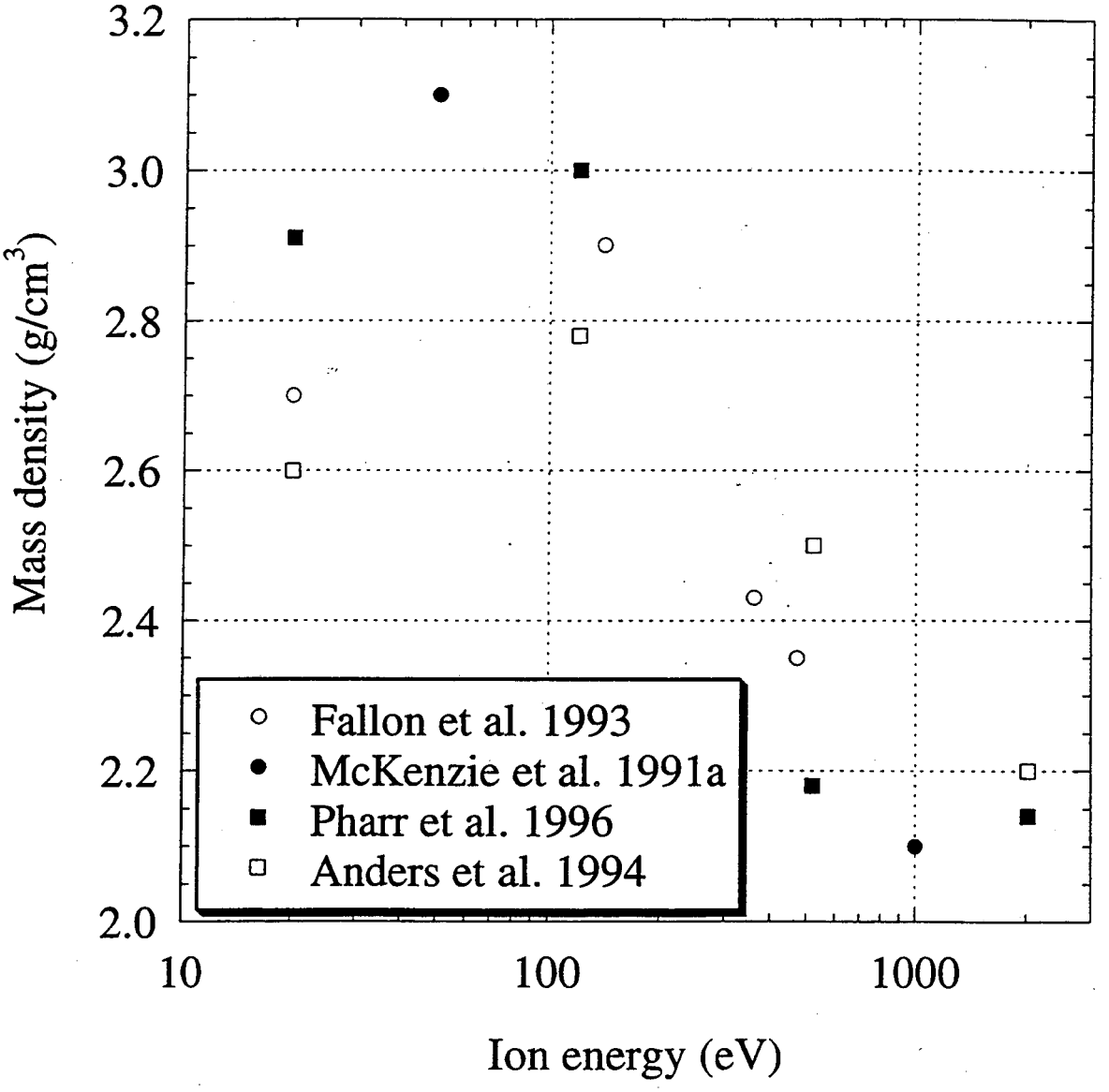
100
1000
Ion energy (eV)
Fallon et al. 1993
Pharr et al. 1996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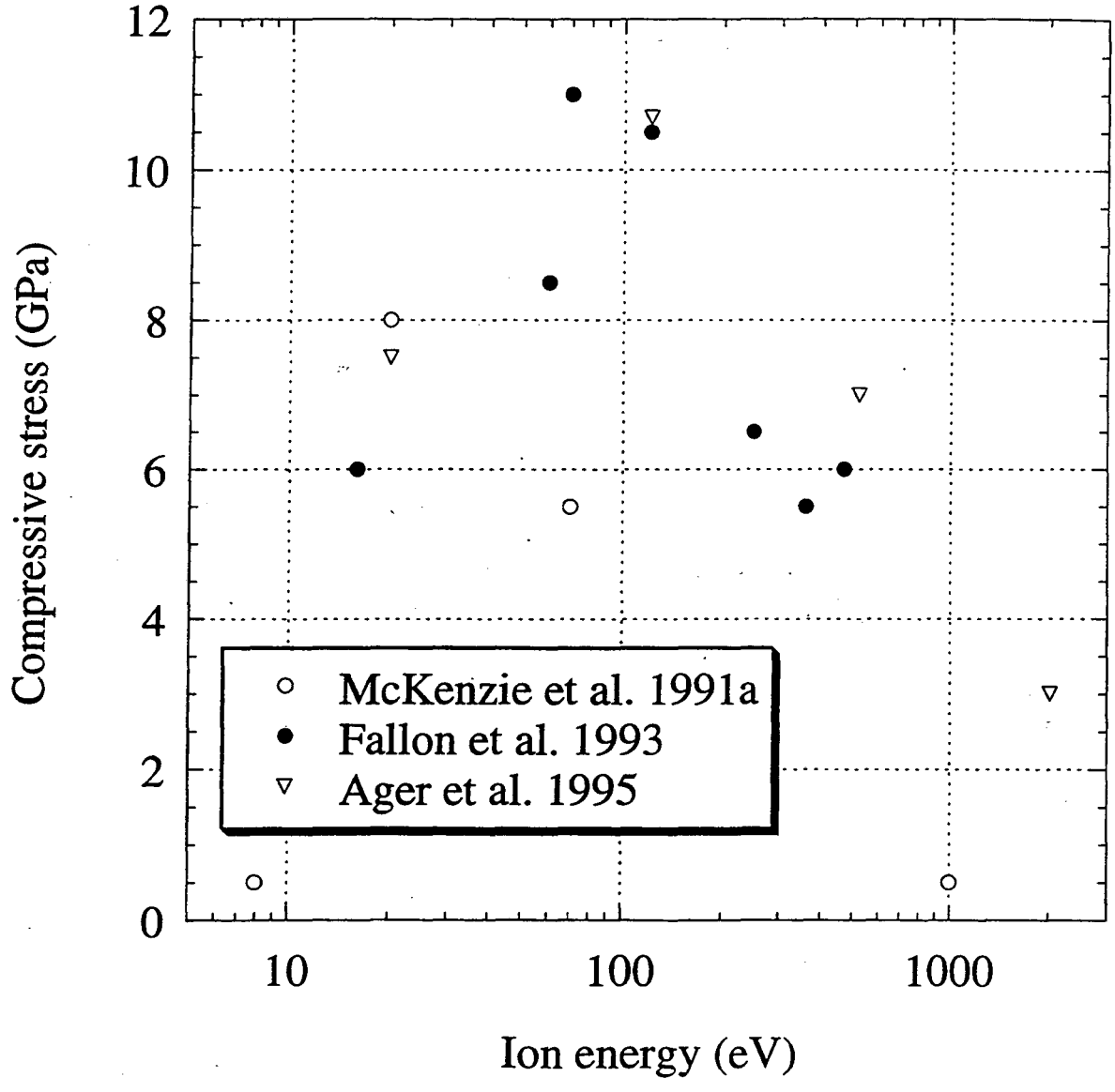
Ion energy (eV)
Fallon et al. 1993
McKenzie et al. 1991a
Pharr et al. 1996
Anders et al. 1994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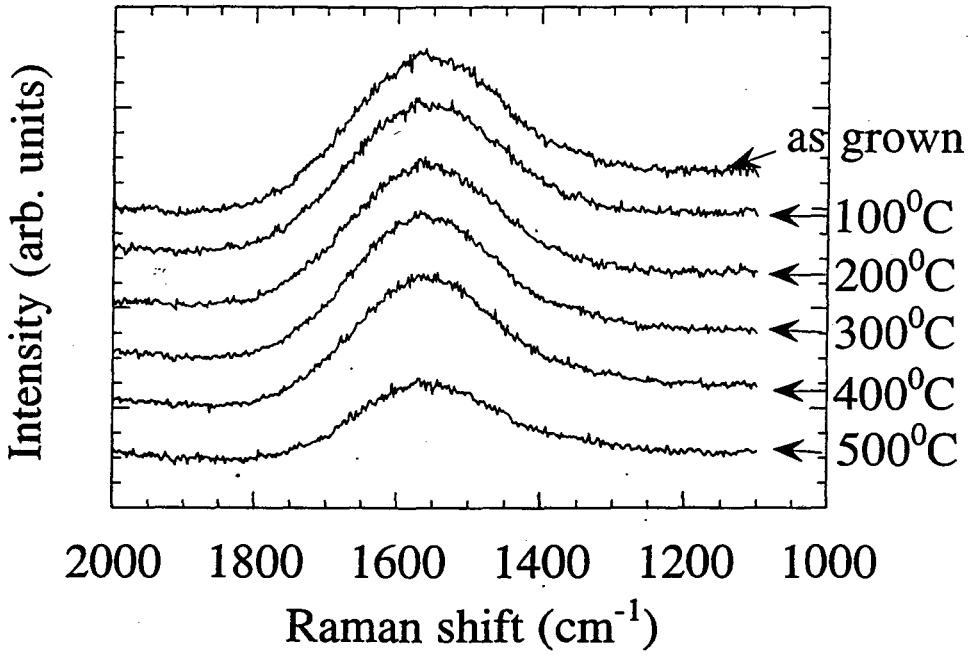
Ager et al. 1995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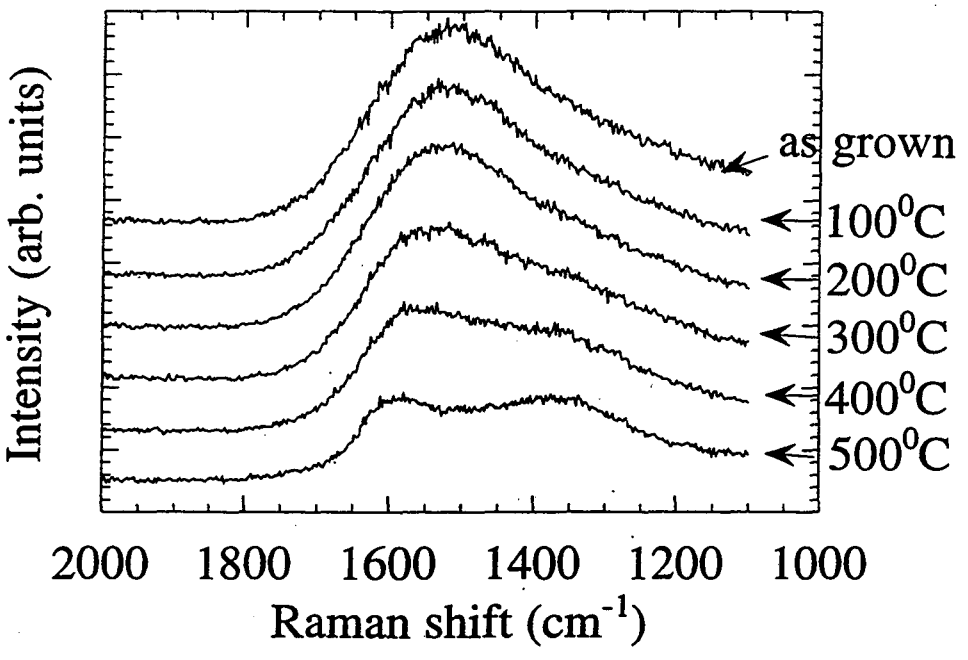
Intensity (arb. units)
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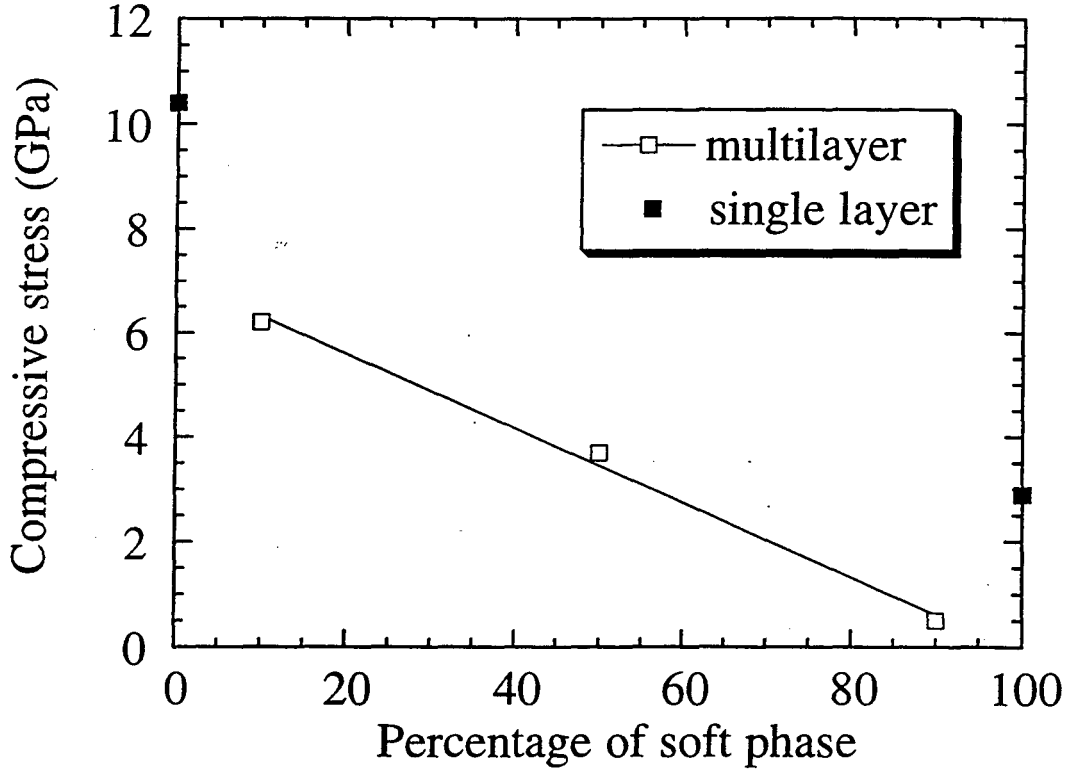
Compressive stress (GPa)
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8
6
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0
0
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40
60
80
100
Percentage of soft phase
multilayer
single layer

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Prepared for the U.S. Department of Energy under Contract No. DE-AC03-76SF00098