Synthesis and Characterization of Pulsed-Laser Deposited Amorphous Carbon Films

Vladimir I. Merkulov[a], Douglas H. Lowndes, G. E. Jellison, Jr.,

A. A. Puretzky, and D. B. Geohegan

Solid State Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831

[a] *Electronic mail*: *merkulov@solid.ssd.ornl.gov*

ABSTRACT

Amorphous carbon films with variable sp^3 content were produced by ArF (193nm) pulsed laser deposition. The film properties were correlated with the kinetic energy of deposited C^+ ions that was measured using an *in-situ* ion probe. Electron energy loss spectroscopy (EELS) and spectroscopic ellipsometry measurements reveal that tetrahedral amorphous carbon (ta-C) films with the most diamond-like properties are obtained at the C^+ ion kinetic energy of ~ 90 eV. Film properties are uniform within a 10-12° angle from the ablation plume centerline. Tapping-mode atomic force microscope measurements show that these energetic-beam-deposited films are extremely smooth, and the films deposited at near-optimum kinetic energy have an rms roughness of only ~ 0.1 nm over distances of several hundred nm.

INTRODUCTION

Hard amorphous carbon films have drawn the attention of the industrial and scientific communities since the first reports on their deposition more than two decades ago [1, 2]. More recent studies have focused on hydrogen-free amorphous diamond films (also known as tetrahedral amorphous carbon, ta-C) that have superior diamond-like properties [3, 4] such as high hardness, a large (~ 2 eV) optical (Tauc) band gap and a low coefficient of friction, as well as chemical inertness and excellent thermal stability. In contrast to graphite and diamond, two crystalline forms of C in which the C atoms have either the sp^2, three-fold (graphite) or the sp^3, four-fold (diamond) bonding configuration, amorphous C (a-C) is a mixture of sp^2 and sp^3-bonded C atoms. Conventional a-C prepared by evaporation or sputtering consists mostly of sp^2-bonded C atoms [5]. In contrast, ta-C films contain a large fraction (up to ~ 75-85%) of sp^3-bonded C atoms and are synthesized using a variety of energetic-beam methods [6] including filtered cathodic vacuum arc (FCVA), mass-separated ion beam deposition (MSIBD), and pulsed laser deposition (PLD).

The amount of sp^3 bonding in ta-C and consequently its diamond-like properties depend upon the kinetic energy (KE) of the carbon species being deposited. The early work by Pappas et al. [7] established such a correlation for PLD. Other early experiments using FCVA, PLD, and other methods showed that films with nearly maximal sp^3 content as well as highly diamond-like properties could be produced using carbon ions whose KE ranged from ~20 eV to at least several hundred eV[6]. For FCVA it recently was established that the highest sp^3 fraction is obtained for C ions with KE of ~ 80-100 eV [8, 9, 10]. Similarly, recent PLD experiments in our laboratory [11, 12] show that the sp^3-bonded fraction, film density, and optical (Tauc) band gap all reach their maximum values for incident carbon ion kinetic energies of ~ 90 eV. In PLD, studies of

diamondlike properties of a-C films as a function of the incident C ion kinetic energy, measured by an *in-situ* ion probe, are advantageous over the measurements that have more often been made as a function of laser fluence. The laser fluence is rather difficult to determine accurately because of (i) a typically large error in measuring the area of the laser spot on the target, (ii) the often unknown attenuation of the beam intensity due to contamination of the vacuum chamber windows. In contrast, *in-situ* ion probe measurements are a substantially more accurate, as well as convenient and fundamental, method for monitoring deposition conditions, with the advantage of being readily transferable for inter-laboratory comparisons. In addition, ion probe measurements can easily detect undesirable changes in experimental conditions (moving optics, target degradation, etc.) during the film growth because the C ion KE is altered by these changes. In this paper we summarize the results of our previous work and also report additional data on the systematic study of changes in the bonding, optical properties, and surface morphology of PLD ta-C films as a function of the C^+ ion KE.

EXPERIMENTAL

ta-C films were prepared in a high vacuum chamber with a base pressure of 4 x 10^{-6} Pa using a Lambda Physik Compex 301i pulsed excimer laser operated with ArF (193 nm). ArF PLD is advantageous over longer wavelengths for deposition of ta-C in that it requires lower energy fluences to produce high quality films [12]. In addition, the ablated flux in ArF PLD consists mostly of *mono*atomic C species even at relatively low fluences [13] which allows for simpler characterization of deposition conditions and direct conversion of the ion current signal to a kinetic energy. Maximum laser fluences at the target were ~ 8 J/cm^2 and produced C^+ KE ~ 100 eV. Higher energy carbon ions were produced using a Questek 2960 excimer laser. The Questek has shorter pulse duration, higher pulse energy, and a sharply peaked beam profile which

allowed C^+ ions to be produced with kinetic energies up to 225 eV. 2.54-cm diameter pyrolytic graphite targets containing < 10 ppm total impurities (Specialty Minerals, Inc., Easton, PA) were used. The substrates were kept at room temperature and placed at variable distances (4.8–7.3 cm) from the target. Typical deposition rates were 0.03-0.1 Å/shot. An ion probe [14] was used to determine the kinetic energy of ablated C^+ ions. It consisted of a bare coaxial-cable tip biased at –100 V and mounted on an arm that rotated it in an arc passing through the center of the propagating ablation plume. The time corresponding to the ion current peak ("icp") was used to calculate a velocity and corresponding kinetic energy of C ions, KE_{icp}.

For spectroscopic ellipsometry (SE) and atomic force microscopy (AFM) measurements ~70-200 nm thick ta-C films were deposited on p- and n-type (001)-oriented Si wafers. Surface roughness studies were carried out using a Nanoscope III AFM (Digital Instruments). A tapping rather than contact mode AFM was utilized because SiN tips used for contact-mode measurements are quickly damaged by the extreme hardness of ta-C films, resulting in degraded image quality. The SE measurements were made using the two-modulator generalized ellipsometer (2-MGE) [15] operating from 250 to 850 nm. The SE results were fit using a 5-medium model consisting of air/ surface roughness/ ta-C film/ interface/ Si, and the optical properties of ta-C films were modeled using the 5-parameter Tauc-Lorentz (TL) formulation for the optical functions of amorphous materials [16]. Previous studies [17] have shown that this model does a superior job of fitting SE data taken on a wide range of amorphous materials, yielding the thickness of each layer, the Tauc (optical) band gap, and the optical functions of the film.

For EELS measurements ta-C was deposited on freshly cleaved NaCl substrates which were subsequently dissolved in DI water. The resultant free-standing ta-C films were placed on folding Ni TEM grids. The thickness of the films was ~ 30 nm which is substantially lower than

the mean free path for 100 keV electrons (> 50 nm). In this case the effect of multiple scattering can be neglected. The EELS measurments were carried out using a VG HB501 STEM fitted with a high sensitivity parallel EELS and operated at 100 keV. The energy resolution was 1.1 eV during the measurements, as determined by the FWHM of the zero-loss peak. We did not observe any notable degradation or contamination of the specimens throughout the experiments.

RESULTS AND DISCUSSION

The energy distribution of carbon ions produced by PLD is quite wide (FWHM ~ 50%). Nevertheless, the ion current peak of the ion probe signal and the corresponding kinetic energy (KE_{icp}) are sufficiently well defined to carry out studies of systematic changes in a-C film properties as KE_{icp} is varied. Fig. 1 compares the C^+ ion kinetic energies produced by KrF (248 nm) and ArF (193 nm) laser ablation using the same experimental setup and focused spot size (only moving the spherical lens to keep the target at the focal point). Clearly, the ArF laser has an advantage in producing higher kinetic energies than KrF at any given fluence.

EELS measurements were used to study the kinetic energy dependence of the amount of sp^3 bonding and the density of PLD C films. The K-edge spectra of a-C films deposited by ArF PLD with various C^+ ion kinetic energies (corresponding to the ion current peak) are shown in Fig. 2a. The spectra exhibit two main features: a peak at ~ 285 eV and a broad band with a maximum at ~ 293 eV. These features are due to 1s-π* and 1s-σ* electronic transitions, respectively [18]. The former is associated with sp^2-bonded C atoms and the latter with both sp^2 and sp^3 C atoms. One can see that the relative intensity of the 1s-π* peak changes with the C ion KE_{icp} and becomes the lowest for the films prepared with KE_{icp} in the range of 70-120 eV. This corresponds to the materials with the lowest sp^2 content and hence more diamond-like properties. EELS spectra also were measured in the low-energy range and are shown in Fig. 2b. The broad

peak around 30 eV is associated with collective excitation, or a plasmon, of the valence electrons[18]. Using a simple Drude-like model, the energy of this plasmon is proportional to the density of ta-C films[19]. As two film-density reference points one can use the plasmon peak positions of graphite (~26.5 eV) and of diamond (33.6 eV).

The analysis of the sp^3 fractions in the ta-C films was performed in a way similar to that of Berger et al. [18] and is described elsewhere [11]. Briefly, the sp^2 fraction, f_{sp^2}, is calculated by taking the ratio of integrated intensities of the 1s-π* and 1s-σ* peaks, I_π / I_σ, and by comparing it to that of arc-evaporated a-C, which is assumed to be entirely sp^2 bonded. The sp^3 fraction is then simply 1-f_{sp^2}. There are quite a few uncertainties in the data analysis and interpretation associated with this method [11]. The difficulty of sample preparation is also an issue. In spite of these problems, EELS is currently the most-used tool for analyzing the sp^3 fraction in ta-C. Partly this is due to the absence of any more suitable alternative method, although uv Raman scattering may be a good candidate. In contrast to conventional Raman scattering in the visible, uv Raman scattering directly reveals the presence of sp^3-bonded C atoms [20, 21] and therefore provides a potential means of simple, nondestructive characterization of ta-C films. We believe that a combination of techniques, such as EELS, ellipsometry, Raman scattering, and possibly others, is required to fully characterize such a complicated material as ta-C. Nevertheless, EELS provides a reasonable sp^3 estimate suitable for most practical applications.

The extracted sp^3 fractions as a function of C ion KE_{icp} are shown in Fig. 3a. The sp^3 fraction clearly exhibits a maximum of ~ 73% at KE_{icp} ~ 90 eV. This is consistent with the optimum KE obtained for FCVA deposition of ta-C. Fig. 3b shows that the position of the C plasmon peak also reaches its highest value of ~30.9 eV at KE_{icp} ~ 90 eV. This behavior is expected since higher plasmon peak energy corresponds to higher film density, which is characteristic of more diamond-like films with higher sp^3 content. It should be noted that the plasmon peak position is a more useful tool for correlating the quality of ta-C films obtained by

different research groups than the sp^3 fraction. There may be substantial inter-laboratory discrepancies in the estimate of sp^3 fractions due to several factors, including structural differences in sp^2 calibration samples, variations in the energy ranges and fitting procedures used to define I_π and I_σ, and differences in EELS resolution. The plasmon peak position is a much more settled parameter and therefore is preferable for judging the diamond-like properties of a-C films.

The EELS results were correlated with scanning ellipsometry (SE) measurements of the optical properties of ta-C films. The optical energy gaps extracted from the SE measurements are shown in Fig. 3c as a function of the C ion KE_{icp}. The trend is very similar to that observed for the sp^3 fraction and the plasmon peak position. The energy gap is lower for the films prepared at low KE_{icp}, reaches its maximum at KE_{icp} ~ 90 eV, and decreases for higher values of KE_{icp}. This is consistent with the variation of the sp^3 fraction, since sp^3-rich films are expected to have a larger optical gap (5.5 eV for pure crystalline diamond) and the gap disappears for predominantly sp^2-bonded carbon.

Measurements of the angular distribution of the C^+ KE_{icp} also were carried out since this determines the maximum area within which spatially uniform film properties can be obtained at any given target-substrate separation, D_{ts}. As shown in Fig. 4, KE_{icp} was nearly constant (±10%) within a half-angular range of 10 to 12 degrees on either side of the plume centerline. At D_{ts} = 10 cm, for instance, this corresponds to a ~ 15 cm^2 region of uniform film properties.

Also, SE measurements of ta-C films deposited on 7.5 cm diameter Si wafers were employed to study film properties as a function of distance away from the plume center. It was found that not only film thickness but also the optical energy gap (E_g) varied with distance away from the plume center. This is due to the fact that diamondlike properties are a function of C ion KE which, in turn, depends on the angle from the plume centerline (see Fig. 4). If KE_{icp} at the plume center is not substantially higher than the optimum energy of 90 eV, as shown in Fig. 5a,

then uniform diamond-like properties (E_g ~ constant) result over a large central area with properties changing rapidly only further away. However, if a much higher central KE_{icp} is used, such as in the case of KE_{icp}= 200 eV presented in Fig. 5b, then a *degraded* central area is produced (with E_g *increasing* away from center) surrounded by a ring of the most diamond-like ta-C, with a rapid fall-off in properties still further away. These angular dependences of E_g are consistent with the energy dependence shown in Fig. 3c and the angular distribution of KE_{icp} in Fig. 4 and again confirm the existence of the optimum KE_{icp} of ~ 90 eV for ta-C film deposition.

The AFM images shown in Fig. 6 reveal that ta-C films deposited at KE_{icp} values of 26, 44, and 90 eV all are quite smooth but still display systematic differences in roughness that are correlated with the KE_{icp} of the C ions used for deposition. Films deposited at 90 eV are extremely smooth with an rms roughness of ~0.09nm measured over $(200\ nm)^2$ areas. For 26 and 44 eV the corresponding rms roughness values are ~0.16 nm. Similarly, the Z-range of height variation within the $(200\ nm)^2$ area increases from ~0.09 nm (at 90 eV) to ~0.16 nm (at 26 eV). We note that these energetically deposited carbon films also are relatively free of the large (~ µm scale) particulates sometimes produced by pulsed laser deposition, with typical and largest particulate diameters of ~ 2–10 nm and ~ 100 nm, respectively. The tapping mode AFM results of Fig. 6 are in good agreement with the AFM measurements reported by Lifshitz [6] for ta-C films deposited on silicon substrates by the MSIBD method. Lifshitz found a pronounced increase in roughness for films deposited at a C ion kinetic energy of 10 eV but very smooth films for kinetic energies ranging from 50 eV up to 10 keV.

SUMMARY AND CONCLUSIONS

In conclusion, the combination of ArF pulsed laser deposition and *in-situ* ion probe measurements allows for deposition of ta-C films with well-controlled diamond-like properties. EELS measurements show that both the sp^3 fraction and the plasmon peak energy (~ film

density) reach their maximum values of ~73% and 30.9 eV in films deposited at KE_{icp} ~ 90 eV. Scanning ellipsometry measurements reveal that the optical (Tauc) energy gap is also maximized (~ 2.0 eV) at KE_{icp} ~ 90 eV, consistent with the presence of the highest sp^3 fraction. This combination of independent optical and electronic measurements provides strong evidence of an optimum kinetic energy KE_{icp} ~ 90 eV for ArF PLD of ta-C. Measurements of the angular distribution of C^+ kinetic energy show that films with highly uniform (±10%) diamond-like properties are obtained within a half-angular range of at least 10–12 degrees on either side of the plume centerline. Tapping-mode AFM measurements show that films deposited at near-optimum KE are extremely smooth, with rms roughness of only ~ 0.1 nm over distances of several hundred nm, and are relatively free of particulates. A distinct increase of surface roughness is observed with decreasing C^+ ion KE and is associated with the increase in sp^2-bonding.

ACKNOWLEDGMENTS

The authors thank S. J. Pennycook for making available the STEM with which the EELS measurements were carried out and P. H. Fleming for assistance with sample preparation. This research was partially sponsored by the Defense Advanced Research Projects Agency under [22]contract DARPA-MIPR-97-1357 with Oak Ridge National Laboratory (ORNL), and by the Office of Basic Energy Sciences, Division of Materials Sciences, U. S. Department of Energy. The research was carried out at ORNL, managed by Lockheed Martin Energy Research Corp. for the U. S. Department of Energy, under contract DE-AC05-96OR22464.

REFERENCES

[1] S. Aisenberg and R. Chabot, *J. Appl. Phys*. **42** (1971) 2953

[2] I. I. Aksenov, V. A. Belous, V. G. Podalka, and V. M. Khoroshikh, *Sov. J. Plasma Phys*. **4** (1978) 425

[3] J. Robertson, *Prog. Solid State Chem*. **21** (1991) 199

[4] D. R. McKenzie, Y. Yin, N. A. Marks, C. A. Davis, E. Kravtchinskaia, B. A. Pailthorpe, G. A. J. Amaratunga, *J. Non-Crystalline Solids* **164-166** (1993) 1101

[5] H. Pan, M. Pruski, B. C. Gerstain, F. Li, and J. S. Lannin, *Phys. Rev. B.* **44** (1991) 6741

[6] Y. Lifshitz, *Diamond Relat. Mater*. **5** (1996) 388

[7] D. L. Pappas, K. L. Saenger, J. J. Cuomo, and R. W. Dreyfus, *J. Appl. Phys*. **72** (1992) 3966

[8] S. Ravi, P. Silva, S. Xu, B. X. Tay, H. S. Tan, and W. I. Milne, *Appl. Phys. Lett.* **69** (1996) 491

[9] S. R. P. Silva, S. Xu, B. K. Tay, H. S. Tan, H.-J. Scheibe, M. Chhowalla, and W. I. Milne, *Thin Solid Films* **290-291**, (1996) 317

[10] M. Chhowalla, J. Robertson, C. W. Chen, S. R. P. Silva, C. A. Davis, G. A. J. Amaratunga, and W. I. Milne, *J. Appl. Phys.* **81** (1997) 139

[11] V. I. Merkulov, D. H. Lowndes, G. E. Jellison, Jr., A. A. Puretzky, and D. B. Geohegan, *Appl. Phys. Lett.* **73** (1998) 2591

[12] D. H. Lowndes, V. I. Merkulov, A. A. Puretzky, D. B. Geohegan, G. E. Jellison, Jr., C. M. Rouleau, and T. Thundat, in R. Singh et al. (eds.) *Advances in Laser Ablation of Materials*, Materials Research Society, Warrendale (1998), p. 325

[13] A. A. Puretzky, D. B. Geohegan, G. E. Jellison, M. M. McGibbon, *Appl. Surf. Sci*. **96-98** (1996) 859

[14] D. B. Geohegan, in D. B. Chrisey and G. K. Hubler (eds.) *Pulsed Laser Deposition of Thin Films*, John Wiley & Sons, New York, 1994, p. 124-7 and p. 147-8

[15] G. E. Jellison, Jr., and F. A. Modine, Appl. Opt. **36**, 8184 (1997); G. E. Jellison, Jr., and F. A. Modine, Appl. Opt. **36** (1997) 8190

[16] G. E. Jellison, Jr., and F. A. Modine, Appl. Phys. Lett. **69**, 371 (1996); G. E. Jellison, Jr., and F. A. Modine, *Appl. Phys. Lett.* **69** (1996) 2137

[17] G. E. Jellison, Jr., D. B. Geohegan, D. H. Lowndes, A. A. Puretzky, and V. I. Merkulov, in R. Singh et al. (eds.) *Advances in Laser Ablation of Materials*, Materials Research Society,

Warrendale (1998), p. 349; G. E. Jellison, Jr., F. A. Modine, P. Doshi, and A. Rohatgi, Thin Solid Fims **313-314** (1998) 193

[18] S. D. Berger and D. R. McKenzie, and P. J. Martin, *Phil. Mag. Lett*. **57** (1988) 285

[19] R. F. Egerton, *Electron Energy Loss Spectroscopy in the Electron Microscope*, Plenum, NY, 1986

[20] V. I. Merkulov, J. S. Lannin, C. H. Munro, S. A. Asher, V. S. Veerasamy, and W. I. Milne, *Phys. Rev. Lett.* **78** (1997) 4869

[21] G. Adamopoulos, K. W. R. Gilkes, J. Robertson, N. M. J. Conway, B. Y. Kleinsorge, A. Buckley, D. N. Batchelder, *Diam. Relat. Mater.* **8** (1999) 541

FIGURE CAPTIONS

Figure1. C^+ ion kinetic energies measured at the plume center vs ArF (circles) and KrF (squares) laser power density. The duration of ArF and KrF pulses were 26 and 39 ns, respectively.

Figure 2. EELS K-edge (a) and plasmon (b) spectra of amorphous C films prepared by ArF PLD at various C ion kinetic energies (KE_{icp}) corresponding to the ion current peak of the ion probe signal. The 27 eV spectrum in (a) is decomposed into sp^2 (I_π) and sp^2+sp^3 (I_σ) contributions. The circles and dashed line in (b) indicate changes in the plasmon peak position corresponding to different film densities.

Figure 3. sp^3 content (a) and plasmon peak position (b) extracted from the EELS measurements (Fig. 2) and optical (Tauc) energy gap (c) obtained by scanning ellipsometry, as a function of C ion kinetic energy, KE_{icp}. All the parameters are maximized at KE_{icp} ~ 90 eV.

Figure 4. Angular variation of C^+ ion kinetic energy for ArF (circles) and KrF (squares) laser ablation of pyrolytic graphite. The pulse energy density for ArF and KrF were ~ 8.1 and 26 J/cm^2, respectively.

Figure 5. Spatial variation of film thickness and optical (Tauc) energy gap in a ta-C film deposited at the plume-center KE_{icp} of 126 eV (a) and 200 eV (b).

Figure 6. AFM images of the surfaces of amorphous carbon films deposited at kinetic energies (KE_{icp}) of 26 eV (top), 44 eV (middle), and 90 eV (bottom). [z range = 2 nm]

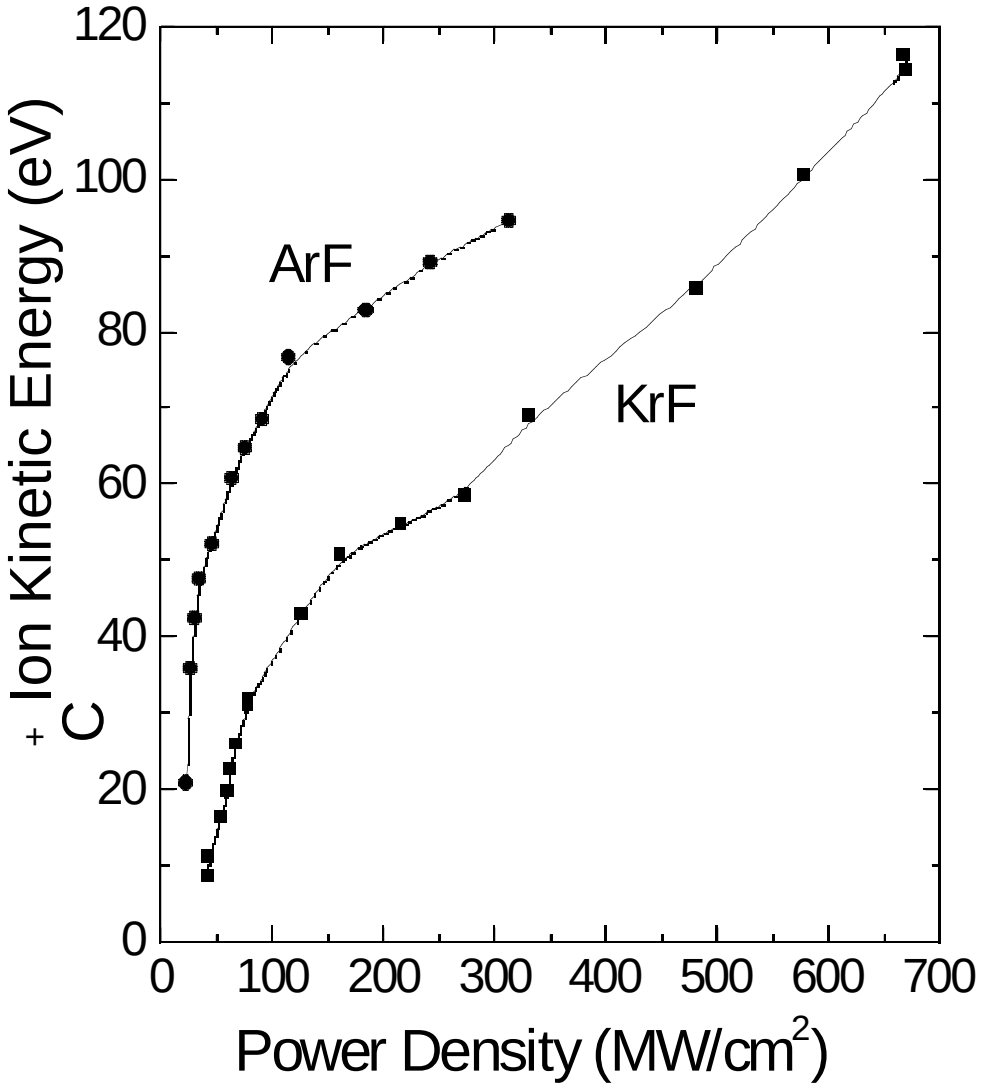

Figure 1. Merkulov et al.

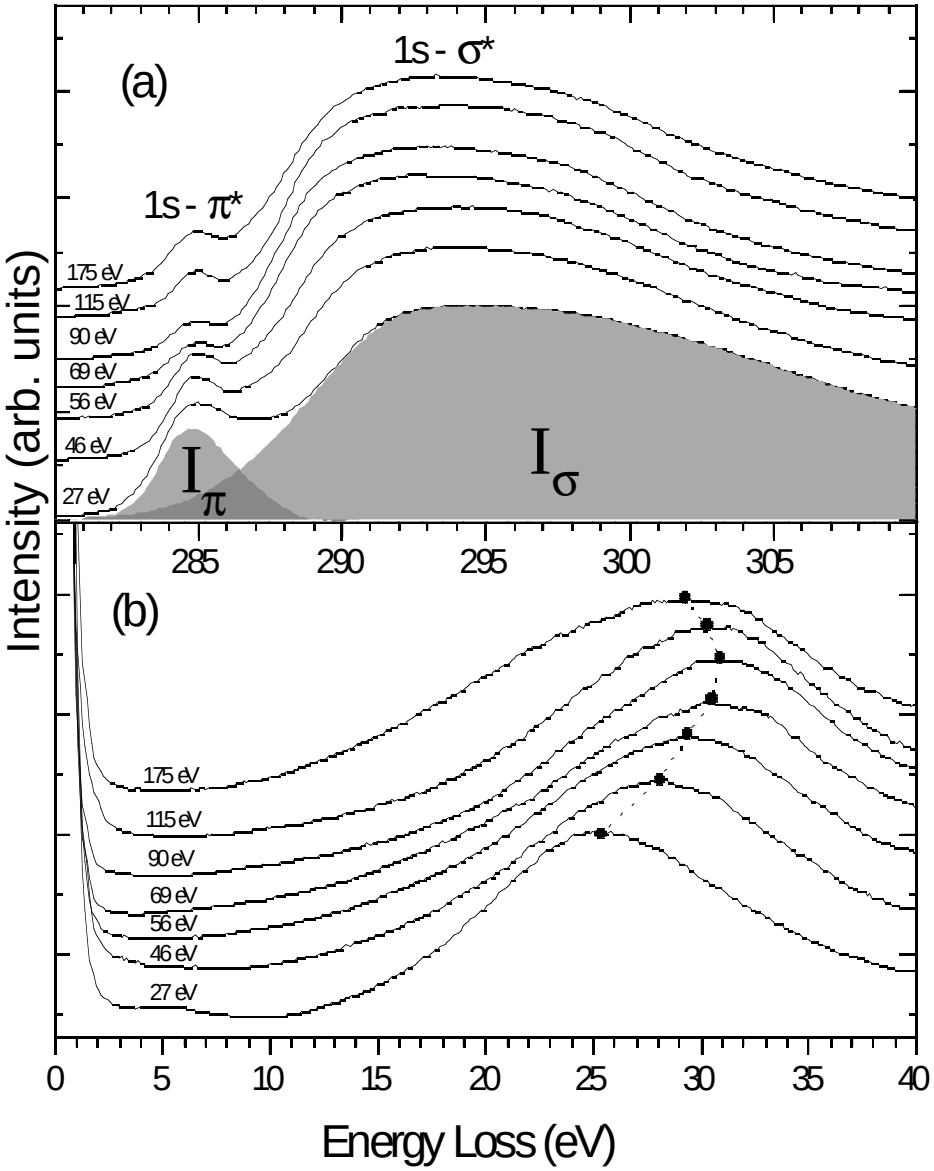

Figure 2. Merkulov et al.

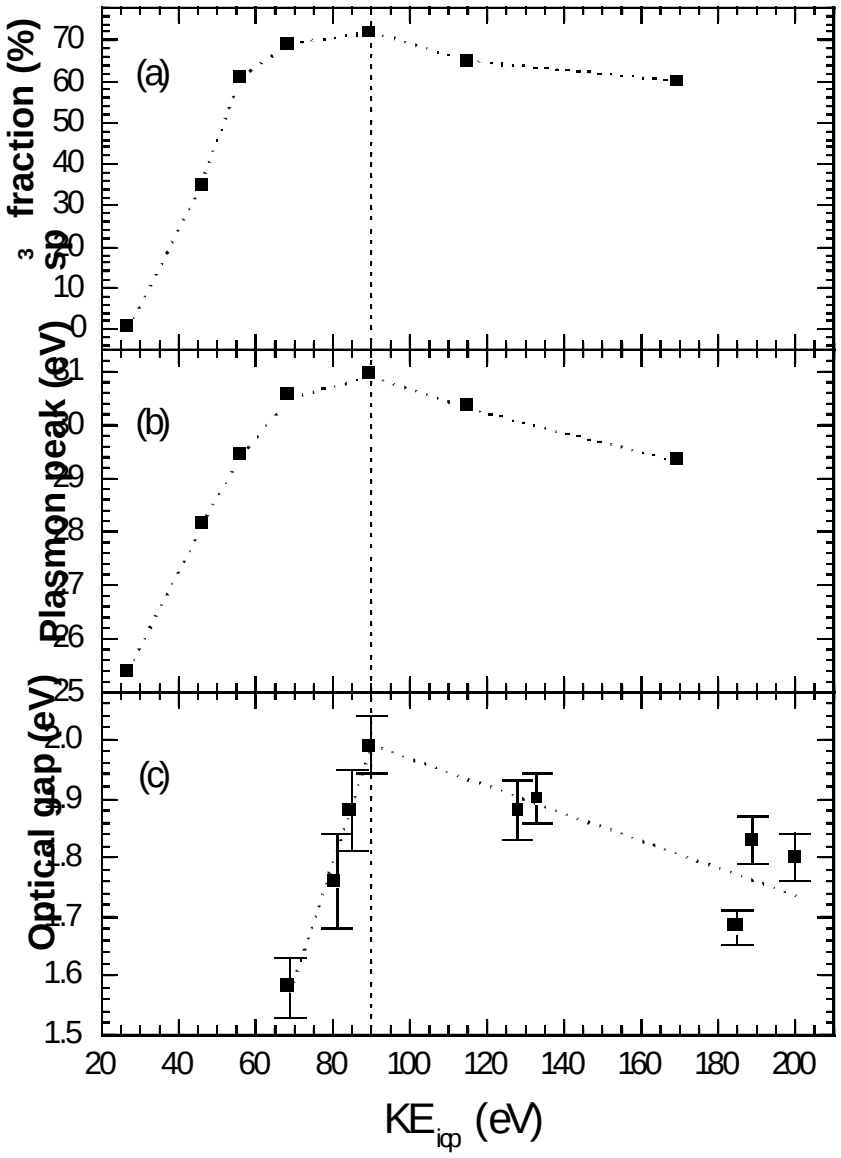

Figure 3. Merkulov et al.

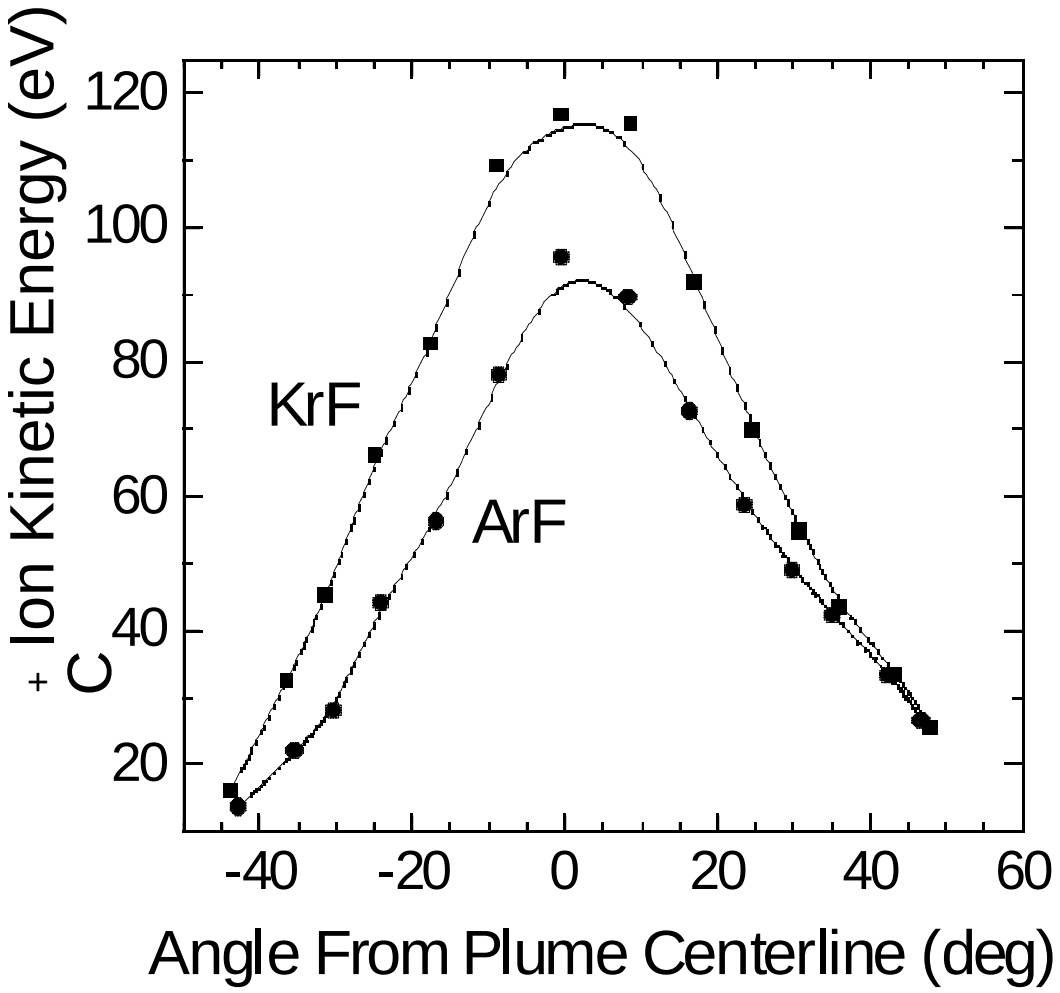

Figure 4. Merkulov et al.

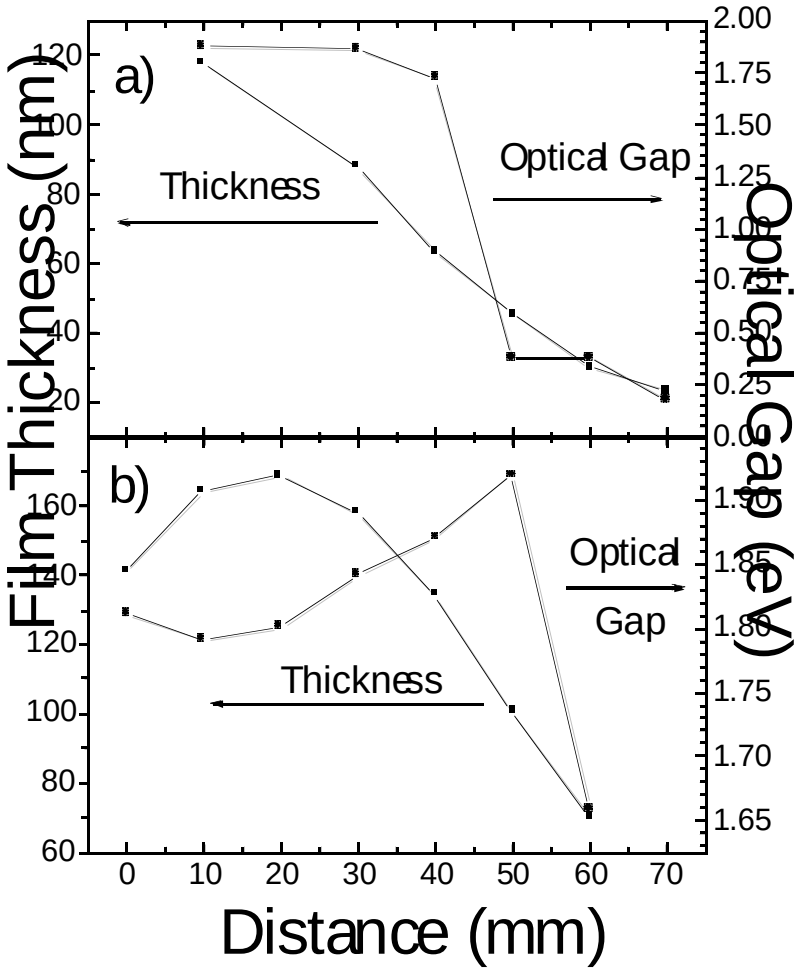

Figure 5. Merkulov et al.

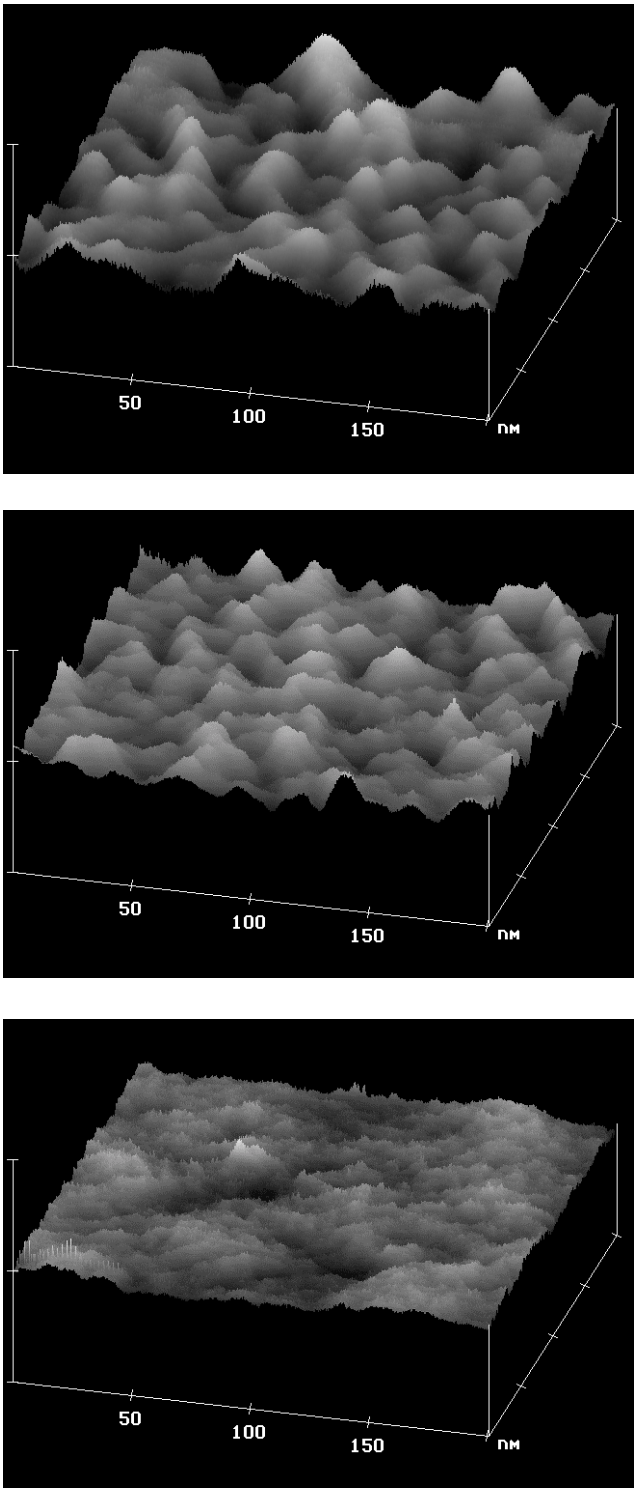

Figure 6. Merkulov et al.