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Heat treatment of cathodic arc deposited amorphous hard carbon films

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Abstract

Amorphous hard carbon films of varying sp^2/sp^3 fractions have been deposited on Si using filtered cathodic arc deposition with pulsed biasing. The films were heat treated in air up to 550°C. Raman investigation and nanoindentation were performed to study the modification of the films caused by the heat treatment. It was found that films containing a high sp^3 fraction sustain their hardness for temperatures at least up to 400°C, their structure for temperatures up to 500°C, and show a low thickness loss during heat treatment. Films containing a low sp^3 fraction graphitize during the heat treatment, show changes in structure and hardness, and a considerable thickness loss.

Introduction

Amorphous hard carbon is a material of great interest for wear protection for its high hardness, low coefficient of friction, and chemical inertness. It has been applied to tools and computer hard disks to reduce wear and increase performance and durability. In tool coating applications, the thermal properties of the coating are important since tools can reach very high temperatures during operation, and the protective coating must not degrade under these conditions. Amorphous hard carbon films are also used as a component of multilayers for X-ray mirrors, and for this application thermal stability of the film properties is of great importance as well.

Cathodic arc deposition is a method to form amorphous, hard, hydrogen-free carbon films of high hardness and sp^3 fraction using pulsed biasing to control the ion energy during deposition. Energy control is the key for the deposition of amorphous hard carbon films which can reach a hardness close to that of diamond and an sp^3 fraction of up to 85% [1]. Properties of these films have been extensively studied by a number of groups [2-8]. These films are deposited usually at or close to room temperature because it was found that an elevated temperature during deposition leads to deterioration of the film properties and eventually graphitization of the films [4]. Elevated deposition temperature causes a more graphitic nature of the deposited films not only for cathodic arc deposition but also for laser ablated [9, 10], ion beam deposited [9, 11, 12], and sputtered films [13].

The thermal behavior of hydrogenated amorphous hard carbon films deposited by various methods has been investigated by a number of authors using Raman spectroscopy [14, 15], Auger and thermal desorption measurements [14], FTIR [16], and stress measurements [16]. The wear behavior of these films has been studied also using friction and wear tests [15, 16] for films annealed in vacuum, air, nitrogen, or boiling water for long durations such as several hours and temperatures up to 600°C, or exposed to rapid thermal annealing for few minutes and temperatures up to 1000°C. In general, the films lose hydrogen, show a more graphitic Raman spectrum (increased intensity of the D-band and shift of the G-band to higher

wave numbers), increased coefficient of friction, increased index of refraction, reduced stress, and increased wear [14-16] - an overall more graphitic behavior. The onset temperature for these effects depends on the deposition method and the annealing conditions, and it is typically between 200 and 500°C.

In contrast to hydrogenated amorphous carbon films, cathodic arc deposited films are less well-studied. The temperature dependence of cathodic arc deposited amorphous carbon films with and without nitrogen doping was studied by McKenzie et al. [17] who found a constant plasmon energy of 28-30 eV for both nitrogen doped and undoped films which were annealed in vacuum for 1 hour up to temperatures of 700°C. In the present paper we describe experiments carried out to study the temperature behavior in air of cathodic arc deposited amorphous hard carbon films.

Experimental

Using cathodic arc deposition with pulsed biasing of the substrate, we have deposited amorphous hard carbon films with a thickness of 450 nm on silicon. The filtered cathodic arc source was operated in a pulsed mode with an arc duration of 5 ms, an arc repetition rate of 1 Hz, and an arc current of 300 A. The source and filter are described in detail in [18]. Different bias voltages were applied to obtain films of various properties. The sample was either at ground potential, at -100V, -500V, or - 2kV with a bias pulse duration of 2 μs and a bias pulse off-time of 6 μs. It was found in earlier investigations [19-22] that films deposited at a bias voltage of -100V show the most "diamond-like" character (i.e., high sp^3 fraction, density, hardness etc.) whereas films deposited at a high bias of - 2kV show the most graphitic character. Table 1 summarizes the previously measured properties of the films used in this study.

The films were heat treated in air for a duration of 2h at the given temperature. The heating and cooling rates at the beginning and end of the experiment were 10 degrees/min. The maximum heat treatment temperature was 550°C. We chose to heat the films in air because

this is the condition which is most important for an application as a wear resistant tool coating.

After the heat treatment the samples were investigated by Raman spectroscopy and by nanoindentation. Raman spectra were obtained using 10 mW of 476 nm laser light. The spot size was ca. 20 microns. The integration time was 3 minutes. The Raman spectrum of cathodic-arc deposited films is a single, broad, asymmetric feature centered at ca. 1550 cm^{-1}. The peak center of this feature was determined by the zero-crossing of the differentiated spectrum. The precision of this procedure, as determined by repeat measurements on the same film, is ± 2 cm^{-1}. After annealing some films became graphitic as evidenced by the appearance of two overlapping peaks in the Raman spectrum (G- and D-bands). In these spectra, the position of the G-peak was determined by fitting to two Gaussian lineshapes.

The films were investigated using nanoindentation techniques [23] to determine the hardness and elastic modulus. The measurements were performed using a sharp Berkovich diamond indenter. Furthermore, the film thickness was measured before and after heat treatment using a stylus type profilometer.

Results

In Figure 1 we have plotted the Raman G-band frequency as a function of heat treatment temperature for films deposited at various pulsed bias voltages. It shows a shift of the G-band frequency to higher wave numbers for the films deposited at ground and - 2kV bias, a smaller shift also to higher wave numbers for the film deposited at -500V bias, and a constant position of the G-band frequency for films deposited at -100V bias. Figures 2 and 3 show the Raman spectra of films deposited at -100V pulsed bias and -2kV pulsed bias after heat treatment at different temperatures. The spectra for the films deposited at -100V show a broad peak (G-band) centered at 1558 cm^{-1} having a constant shape with no change in peak positions except that the total signal is reduced for the films treated at high temperature due to loss in film thickness (this will be analyzed later in this section). The Raman spectra for films

deposited at -2kV show the broad peak (G-band) centered at 1520 cm^{-1} for films treated at low temperatures. For higher temperatures the peak shifts to higher wave numbers (up to 1580 cm^{-1}) and a second peak (D-band) appears at 1350 cm^{-1}. The total signal is decreased also due to loss in film thickness.

The hardness and elastic modulus of the films was measured before and after heat treatment for films deposited at different bias voltage. Figures 4 and 5 show the hardness and elastic modulus of films before heat treatment and after 400 °C treatment for films deposited at -100V and -2kV. As found before (see Table 1) it can be seen that films deposited at -100V exhibit a high hardness and elastic modulus of about 45-50 GPa and about 300 GPa, respectively. These numbers are not absolute values for the films because the influence of the substrate has not been considered. As shown in an earlier measurement [22] the hardness and elastic modulus measured by nanoindentation are a function of the film thickness for films in the hundreds of nm range thickness. Films deposited at - 2kV show a much lower value for the hardness and elastic modulus (about 22 GPa and 240 GPa, respectively). Heat treatment of the films up to 400°C does not change the hardness remarkably and lowers slightly the elastic modulus (in particular for the -2kV films).

Figure 6 shows the loss in film thickness as a function of heating temperature for films deposited at -100V and - 2kV with a thickness of 450 nm. Films deposited at - 2kV start to lose thickness above 450°C and are practically completely gone at 475°C. For films deposited at -100V the thickness loss becomes remarkable above 500°C. These films are completely lost for temperatures of 550°C.

Discussion

Raman spectra can give valuable qualitative information about the structure and properties of carbon films. Tamor and Vassell have collected and analyzed a variety of Raman data from different hydrogenated and non-hydrogenated amorphous hard carbon films

deposited by various methods [24]. Whereas Raman spectrum features like G-band position and I_D/I_G ratio are well correlated to film properties such as hardness and density for hydrogenated films, there are not yet sufficient data available to perform similar predictions for non-hydrogenated films without any additional information. Trends found for hydrogenated films cannot be applied automatically to non-hydrogenated films because in some cases the behavior is just the opposite (e.g., the optical gap decreases with increasing G-band position for hydrogenated films whereas it seems to increase for non-hydrogenated films). Nevertheless, we can conclude a number of results from the observed spectra.

Both figures 1 and 2 demonstrate that the films deposited at -100V pulsed have an unchanged Raman spectrum before and after heat treatment. The decrease in intensity in Fig. 2 is attributed to a decrease in in the film thickness, the films get thinner without changing their structure. This is evidence of the high thermal stability of these films. The decrease in the films thickness can be attributed to oxidation. The films deposited at lower and in particular at higher bias voltage than -100V show changes in the Raman spectra. The position of the G-band is shifted to higher values. The D-band appears (which is practically absent in the film deposited at -100V bias) and its intensity rises with increasing heat treatment temperature. The appearance and rising intensity with increasing heat treatment temperature is an indication for a graphitization since the D-band is a well-known feature of the graphite spectrum. The films also lose thickness which is reflected in the reduced intensity of the Raman signal in Fig. 3.

For cathodic arc deposited amorphous carbon films we found that the position of the G-band in the Raman spectrum is correlated to (at least) two film properties - the sp^2/sp^3ratio [19] and the film stress [21]. Comparing Fig. 1 for as grown films and table 1 we can see that a high sp^3 fraction is correlated with a high G-band frequency of 1558 cm^{-1} whereas low sp^3 fraction films have a low frequency of about 1520 cm^{-1}. This is in contrast to observations for hydrogenated amorphous carbon films [25, 26] which show a shift of the G-band frequency to smaller wavelength with higher sp^3 content. It is also in contrast to model calculations [27, 28]

which predict a shift of the G-band frequency to smaller wavelength with higher sp^3 content. Only part of this discrepancy can be attributed to the effects of compressive residual stress. Referring to Table 1 and using our previously measured stress shift value of 1.9 cm^{-1}/GPa [21], the -100 V film peak is shifted to higher frequency by 20 cm^{-1}, while the -2kV film peak is shifted by 6 cm^{-1}. Thus, stress effects can explain only ca. 14 cm^{-1} of the observed 38 cm^{-1} difference between the peak centers of the -100 V and -2 kV films. We do not have a good explanation for the observed increase in G-band frequency with increasing sp^3 content observed in the cathodic-arc films. It is possible that resonance effects in the Raman spectrum, which are not considered by the calculations, might be responsible for the observed trend.

The shift of the G-band frequency to higher values with increased annealing temperature and the appearance of the D-band have been observed by other authors also for hydrogenated, direct ion beam deposited films which where exposed to a Rapid Thermal Annealing process [15] and for hydrogenated CVD deposited films which where heated in vacuum up to 450°C [14]. In both cases as well as for our films this change in the Raman spectrum indicates graphitization of the films.

The hardness and elastic modulus measurements show that the films deposited at -100V remain very hard after heat treatment up to 400°C. Films treated at higher were too thin to perform meaningful nanoindentation measurements because the results are a function of film thickness. Hardness and elastic modulus of films which were deposited at - 2kV bias do not change when comparing as grown and 400°C heat treated films although the Raman spectrum shows a modification of the film structure. This is probably due to the fact that Raman is more surface sensitive (probing depth < 50 nm) whereas nanoindentation is averaging over the contact depth and is further influenced by the underlying substrate to at least one or two times the contact depth.

Conclusions

Amorphous hard carbon films deposited using filtered cathodic arc deposition with pulsed biasing of -100V exhibit a high resistance to heat treatment in air. They sustain their hardness at least up to 400°C and their structure up to 500°C. Raman investigation shows a shift of the G-band frequency to higher values and an increase of the D-band intensity for films which have a low sp^3 fraction (films deposited at no bias or a bias of -500V or higher), and no change in the Raman spectra (except total intensity decrease due to loss in film thickness) for films deposited at -100V. Films deposited at -100V exhibit a lower oxidation rate (loss rate) during heat treatment than films deposited at no bias or a bias of -500V or higher.

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Table 1. Properties of cathodic arc deposited amorphous hard carbon film as a function of the pulsed bias voltage.

Property	Bias voltage (V)	Hardness (GPa)	Elastic modulus (GPa)	Mass density (g/cm^3)	sp^3 fraction (%)	stress (GPa)	coefficient of friction
	0			2.91	81	7.5	0.15
	-100	60	400	3.00	85	10.5	0.10
	-500			2.18	47	7	0.12
	-2000	23	245	2.14	39	3.0	0.16
Reference		20, 22	20, 22	22	22	21	19

Captions for Figures

Fig. 1: Raman G-band frequency as a function of heat treatment temperature for films deposited at various pulsed bias voltages.

Fig. 2: Raman spectra of films deposited at -100V pulsed bias after heat treatment at different temperatures. The spectra have been offset for clarity.

Fig. 3: Raman spectra of films deposited at -2kV pulsed bias after heat treatment at different temperatures. The spectra have been offset for clarity.

Fig. 4: Hardness of films before heat treatment and after 400 °C treatment for films deposited at -100V and -2kV.

Fig. 5: Elastic modulus of films before heat treatment and after 400 °C treatment for films deposited at -100V and -2kV.

Fig. 6: Loss in film thickness as a function of heating temperature for films deposited at -100V and - 2kV with an initial thickness of 450 nm.

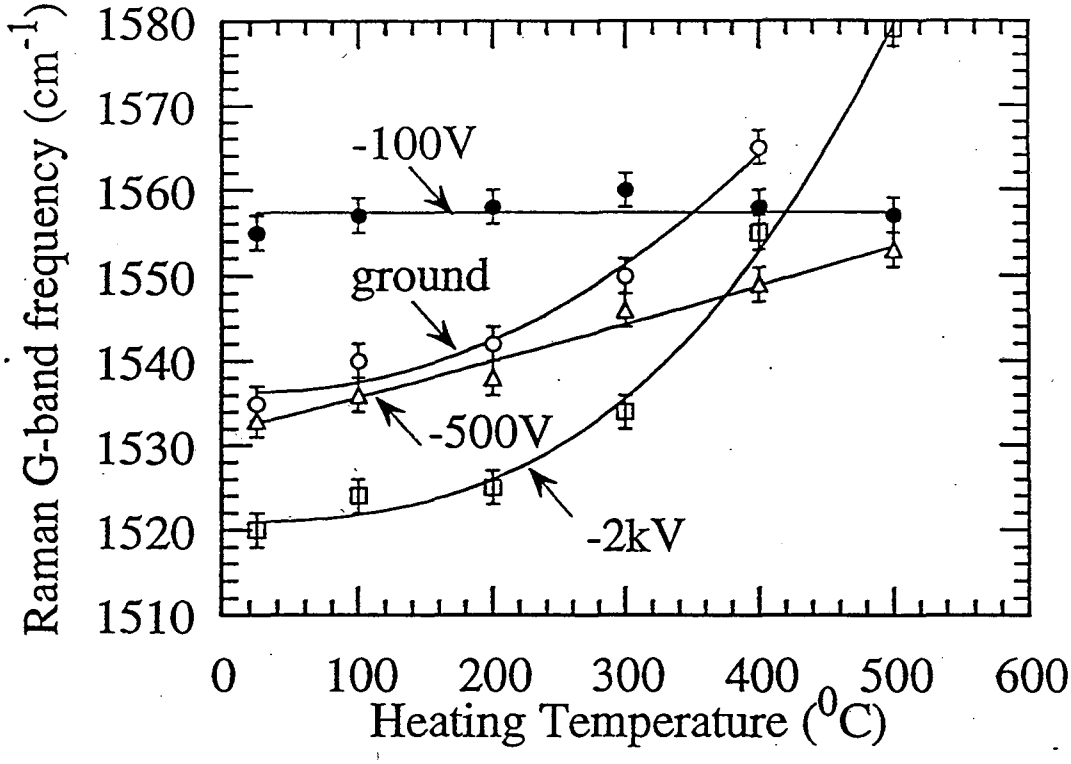
Raman G-band frequency (cm-1)
1580
1570
1560
1550
1540
1530
1520
1510
-100V
ground
-500V
-2kV
0
100
200
300
400
500
600
Heating Temperature (0C)

Fig. 1

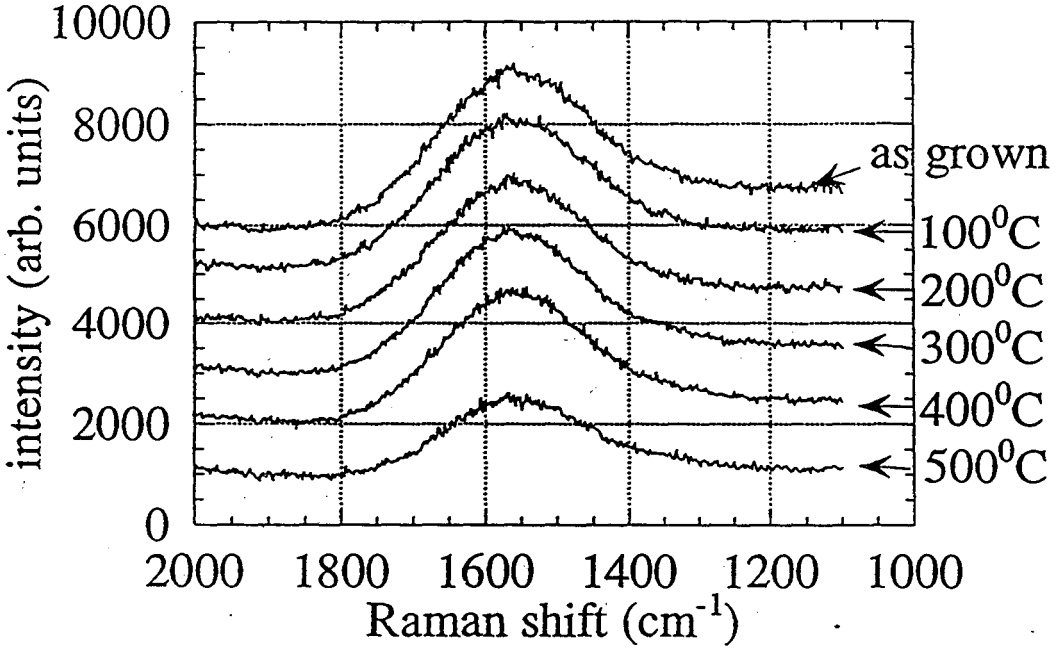
10000
8000
6000
4000
2000
0
intensity (arb. units)
2000
1800
1600
1400
1200
1000
Raman shift (cm-1)
as grown
100⁰C
200⁰C
300⁰C
400⁰C
500⁰C

Fig. 2

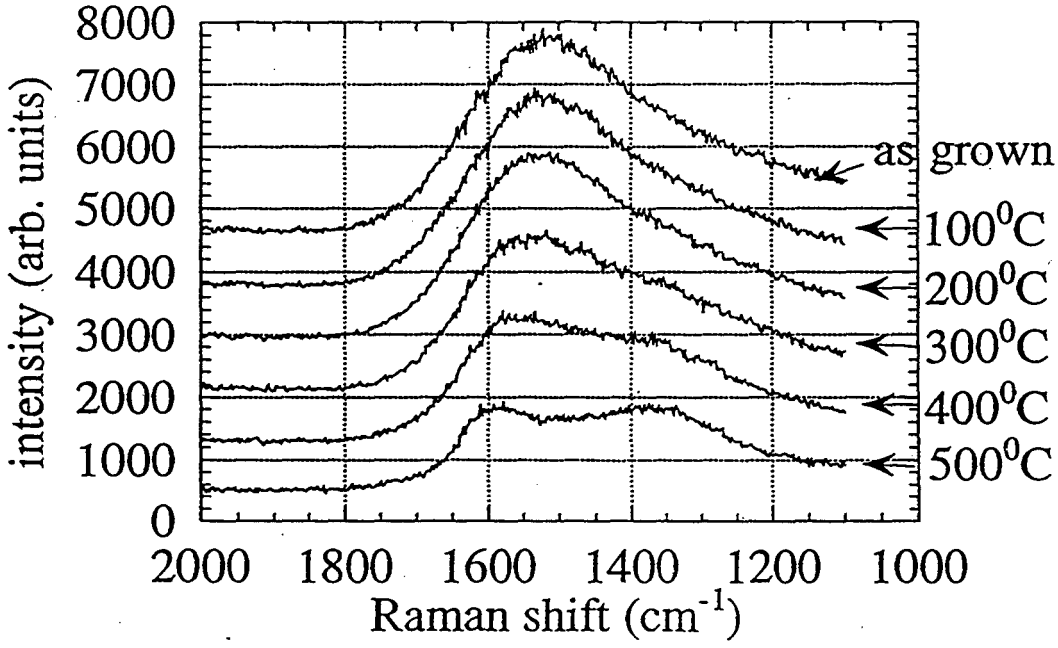
8000
7000
6000
5000
4000
3000
2000
1000
0
intensity (arb. units)
2000
1800
1600
1400
1200
1000
Raman shift (cm-1)
as grown
100°C
200°C
300°C
400°C
500°C

Fig. 3

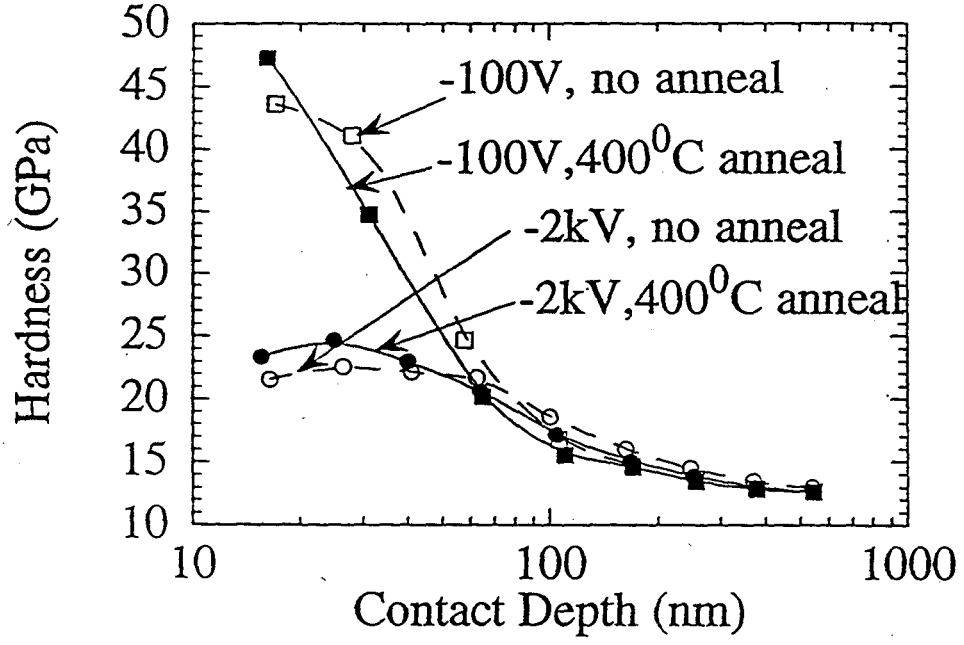
50
45
40
35
30
25
20
15
10
Hardness (GPa)
10
100
1000
Contact Depth (nm)
-100V, no anneal
-100V,400^{0}C anneal
-2kV, no anneal
-2kV,400^{0}C anneal

Fig. 4

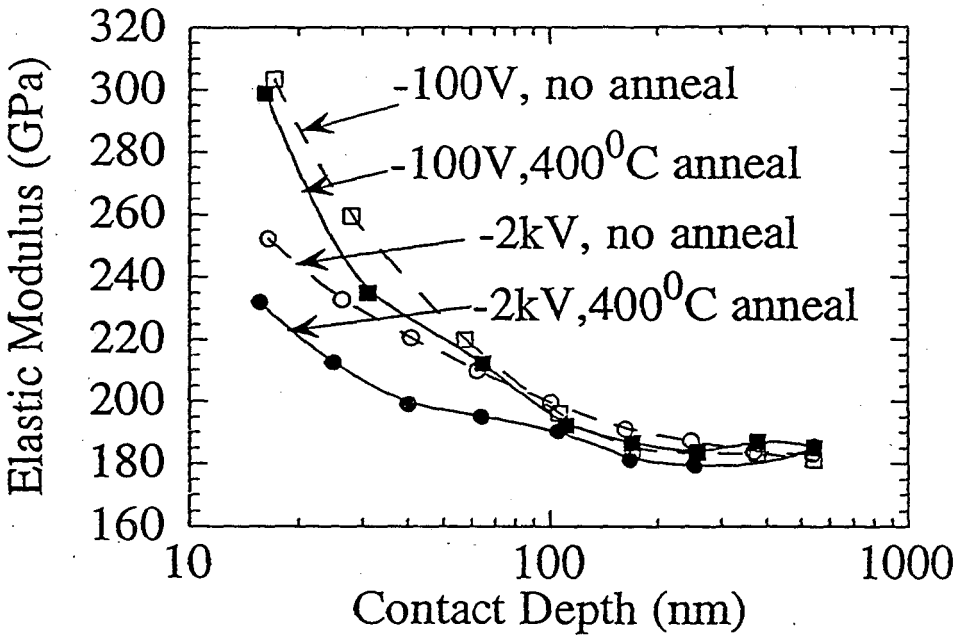
320
300
280
260
240
220
200
180
160
Elastic Modulus (GPa)
10
100
1000
Contact Depth (nm)
-100V, no anneal
-100V,400^{0}C anneal
-2kV, no anneal
-2kV,400^{0}C anneal

Fig. 5

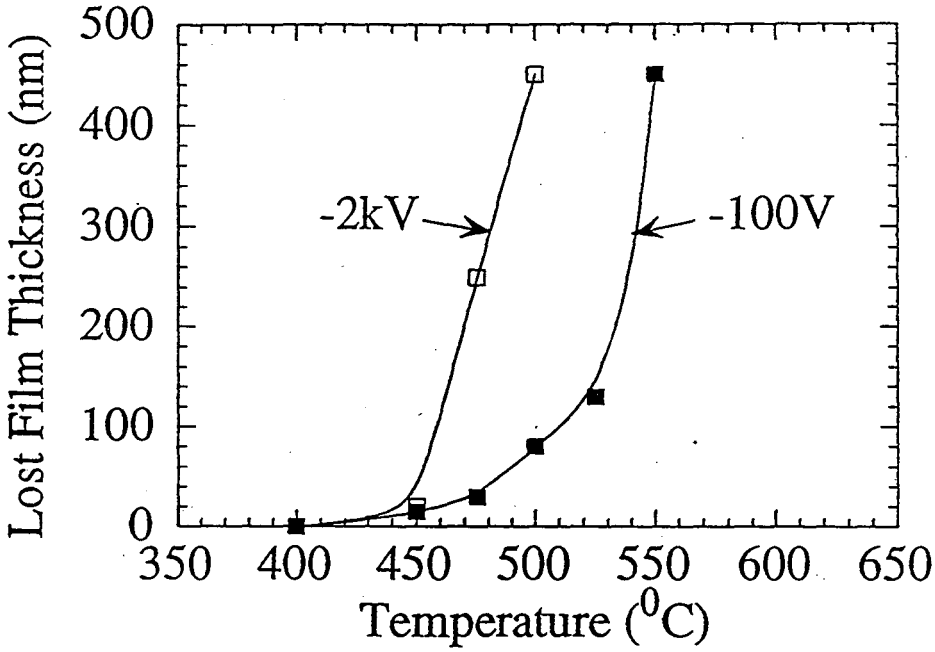
Lost Film Thickness (nm)
500
400
300
200
100
0
350
400
450
500
550
600
650
Temperature (^{0}C)
-2kV
-100V

Fig. 6

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