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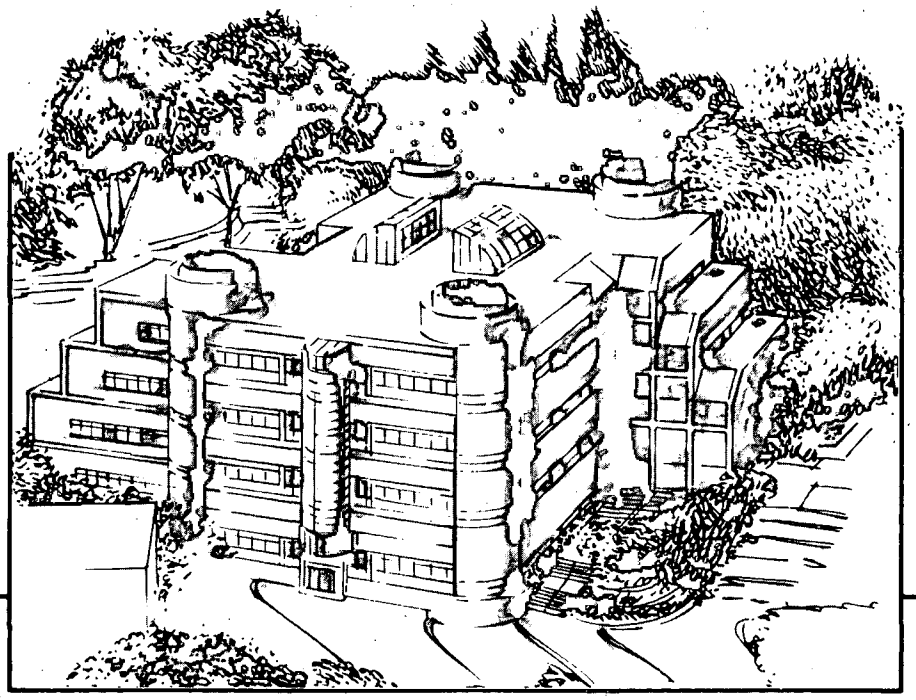

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The effect of ion energy flux on the properties of hydrogenated amorphous carbon films

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Abstract

In this study the effect of varying ion energy flux on the properties of amorphous hydrogenated carbon films produced by plasma assisted chemical vapor deposition from methane was investigated. The ion current, used to calculate the apparent ion energy flux, was measured through an orifice in one of the electrodes of the parallel plate system, using a faraday cup. The film properties investigated include hardness, stress, methyl and methylene concentrations, and optical gap. All the observed properties vary significantly with ion energy flux and are strongly correlated with each other. As ion energy flux increases, the hardness increases, the compressive stress increases, the concentrations of methyl and methylene groups decrease, and the optical gap decreases. The results demonstrate how the ion energy flux on to the film surface controls the final properties of the films.

1 INTRODUCTION

Amorphous hydrogenated carbon (a-C:H) films are the subject of many investigations[1,2] largely because of their useful mechanical, optical, and electrical properties. The films are often synthesized by plasma assisted chemical vapor deposition (PACVD), ion-beam deposition, and sputter deposition. A better understanding of the mechanism of formation of these films is desirable so that better control over the final film properties can be achieved.

In previous studies of the formation of a-C:H films from methane by PACVD[3,4], the results suggested a mechanism involving complimentary roles of ions and radicals. The radicals were demonstrated to be the precursor species responsible for the bulk mass deposition of the films, while the ions were shown to control the mechanical properties. The mechanical properties of the films were shown to vary with the average potential drop between the film surface and the plasma. This parameter was noted to be proportional to the total power supplied by ions to the growing film surface, assuming ion flux to be constant. Thus the control of film hardness by the apparent energy flux of ions to the film surface was suggested.

In this study, the effect of apparent energy flux of ions on the film hardness was investigated more directly using measured values for ion current. Also investigated was the dependance of the optical gap of the films, and the concentrations of methylene ($-CH_2-$) and methyl ($-CH_3$) groups on apparent ion energy flux. The controlling effect of impinging ion energy flux on the final properties of the films is clearly demonstrated. Hardness increases with ion energy flux. The concentrations of methylene and methyl groups in the films decrease with increasing energy flux. The optical gap of the films decreases with increasing ion energy flux. The absolute ion flux measured is an upper limit on the true ion flux and the values obtained demonstrate that the flux of ions is insufficient for ions to be the main precursor species responsible for the bulk mass deposition of the films. This is consistent with the conclusion reached in previous work[3], that the reactive plasma species responsible for the bulk mass deposition of the films are radicals and not ions.

2 EXPERIMENTAL PROCEDURES

The films studied here were produced by PACVD in a parallel plate electrode system described previously[3]. As in the previous work, single crystal silicon(100) wafers were used as substrates, after being etched in 49% HF. In addition, quartz plates were used for optical gap measurement. Methane was used as the feedgas, at a flow rate of $8cm^3/min.$ and a preignition pressure of 65mTorr. In order to control the ion energy flux, a high voltage pulse generator system[3] was used for negative pulsed biasing of the otherwise grounded electrode.

The experimental setup used to measure the plasma ion flux incident on the lower electrode is shown in figure 1. A small hollowed cylindrical electrode was screwed into a glass tube, which held it about 5 mm below an orifice (0.35mm in diameter) located in the lower electrode. The pressure below the electrode orifice was maintained on the order of 10^{-6} torr. In order to attract the positive ions incident on the orifice area, and to repel plasma electrons, a bias voltage of -200 to -800 V was applied to the ion collector. The area of acceptance of the ion collector was large enough to collect the ions effectively, however, the geometry is not optimal for minimizing the loss of secondary electrons, which could contribute to the measured current. Thus, the current measured using this system is, in effect, an upper limit on the real ion current.

The steady state current was measured using a digital D.C. ammeter. An A.C. measurement was also performed, where the potential drop across a standard resistance was monitored with an oscilloscope. By covering the orifice with a shield to block the direct pathway of ions from the plasma to the collector, the background current was first measured, and then subtracted from the current measured without the shield in place. The net current divided by the area of the orifice thus represents an apparent ion flux incident on the lower electrode.

Values measured for ion current increased with increasing faraday cup bias voltage in the voltage range from 0 V to -200 V. This result is not surprising as collection efficiency of positive ions improves and stray electrons are repelled more efficiently as small negative voltages are placed on a faraday cup. The

measured values reached a plateau at faraday cup bias voltages of -200 to -400 V. The values measured at this plateau for ion flux agreed within 20% with measurements made in the AC mode. Overall measured ion current values were reproducible to about $\pm$ 10%. A decrease in the measured values was noticed at bias voltages greater than -600V. The origin of this decrease was not clear, possibly due to a variation in the recollection efficiency of secondary electrons. The values measured at a faraday cup bias voltage of -400 V, in the plateau region, were used exclusively for all the ion energy flux values presented in this paper.

In order to calculate the time averaged ion energy flux from the ion current, possible temporal variations in the ion current must be taken into account. This is especially important for the ion flux measurements for pulsed biasing conditions. The ion current during the high voltage pulse is not necessarily equal to the current between pulses. In this case, the steady state D.C. current could not be used to calculate the average energy flux. To observe the temporal variations of the ion current, the aforementioned A.C. current measurement technique was used.

Figure 2 shows typical oscilloscope traces of the current induced voltage signal across a 1 MΩ resistance, connected between the ion collector and ground. The lower trace in figure 2 shows the signal obtained under no direct ion flow to the collector. Due to a capacitive coupling between the lower electrode and the ion collector, the signal exhibits the same pulse pattern as the applied voltage. When the direct pathway of ions to the collector is opened, the increase of the observed current due to the impinging ions results in an upward shift of the oscilloscope trace as shown in figure 2. It can be seen that the two traces in figure 2 are virtually identical in shape, but simply shifted in the vertical direction. This fact indicates that there is no observable temporal variation of ion flux, even at the pulsed biased electrode. As a result, the calculation of the average ion energy flux is simplified. It is given by the product of the steady state D.C. current density and the time averaged potential drop between the lower electrode and the plasma bulk.

The Knoop hardness of the films was measured with a Buehler Micromet microhardness tester with loads from 5 to 20 g for films thicker than 1 μm. We

used a Clevite Surfanalyser 150 profilometer to measure the film thickness and curvature. From the bending radius, the thickness, and Young's modulus of the substrate, compressive stress of the deposited film can be calculated. The density of the films was determined from the measured mass of the films and their volume. Using transmission FTIR, the methyl and methylene concentrations of the films were determined from the intensities of their respective C-H bending modes at 1375 cm^{-1} and 1460 cm^{-1}, using their respective molecular extinction coefficients (14.9 and 15.0 mol cm, according to the work of Tibbit *et al*[5]). The extinction coefficients are very dependant on local bonding structure, and hence caluculated concentration results should be considered qualitative. The optical transmission spectra for the films were measured with a Perkin Elmer Lambda 9 spectrometer. The optical gap was determined from the Tauc plot[6] of the absorption coefficient by using a linear extrapolation of the absorption edge.

3 RESULTS

3.1 Ion flux measurement

The apparent ion flux was measured for a series of plasma conditions and the results are given in figure 3. At the powered electrode, the apparent ion flux is much greater than at the grounded electrode. It can also be seen that ion flux increases as the pulsed biasing conditions increase in frequency and voltage, however the increase is much less severe. At the greatest frequency and largest pulsed bias voltage, the current has only increased by a factor of about two over that of the grounded electrode.

These values of ion flux can be compared with the deposition rates in terms of number of C_1 species deposited per unit time per unit area. If ions were the main source of deposition species, the ion flux would have to be greater than the C_1 deposition rate. This measurement of ion flux is an upper limit to the real ion flux, as mentioned earlier. Also, the total flux measured contains a large contribution from H^+ and $H_2{}^+$ as measured previously[3]. This is the second factor which requires the measured ion current to be in excess of the deposition rate if ions were the main precursor species for deposition. According to our

previous paper[3], the C_1 species deposition rate at the grounded electrode is about 10^{15} cm^{-2} s^{-1}. At the rf powered electrode the rate is close to 2 x 10^{15} cm^{-2} s^{-1}. The apparent ion flux measured is less than or within experimental variation of the C_1 species flux in both cases. If ions were the main deposition species, the total ion flux would have to be significantly higher than the C_1 deposition rate. This measurement is consistent with our previous conclusion[3], that the bulk mass of the films is mainly supplied by radical species, while the major role of ions is to control the mechanical and chemical properties of the films.

3.2 Effect of average energy flux on a-C:H film properties

The variation of film hardness with pulsed biasing conditions was investigated in a previous paper[3]. However, neither the relative or absolute ion flux values were known, so the time averaged potential drop at the relevant electrode was used as a convenient parameter to represent the power supplied by ions to the growing film surface. The result of the ion flux measurement, as shown in figure 2, makes it possible to reorganize the various biasing conditions in terms of the real energy flux, at least on a relative scale. The apparent ion energy flux was calculated by simply multiplying the time averaged potential drop at the lower electrode by the D.C. current density measured in this experiment. Other important film properties were investigated as a function of this more significant parameter in order to further illuminate the effect of ion energy flux.

The variation of Knoop hardness and compressive stress of a-C:H films as a function of ion energy flux is shown in figure 4. In contrast to the previous representation[3], where the same data were plotted vs. the average potential drop, the solid line approximating the behaviour of the data points is a convex line. Consequently, as shown in the inset of figure 4, the curves can be extrapolated far down to the high energy flux values of hardness and compressive stress which were measured for the films formed at the powered electrode. In the previous paper we emphasized that the mechanical properties of the films are controlled by the power supplied to the film surface by ions but not on the

energy of the individual ions. Figure 4 not only reconfirms this fact but also suggests that it holds over a much wider range of energy flux.

FTIR spectra of the films were measured as a function of biasing conditions in order to investigate how the C-H bonding in the films varied with energy flux. The concentrations of methylene ($-CH_2-$) and methyl ($-CH_3$) groups were determined from the FTIR spectra and are plotted versus energy flux in figure 5. The concentrations of both methylene and methyl groups in the films show a rapid decrease with the energy flux and level off almost completely at a relatively small value of energy flux of about 4 mJ $cm^{-2}s^{-1}$ The methyl group concentration has decreased to near zero at this point, suggesting that most of the crosslinking, which acts to expand a three dimensional amorphous network, has been completed at this value of energy flux. It is interesting to note that it is at this point that the compressive stress of the films begins to increase, as can be seen in figure 4.

The optical gap of the a-C:H films was measured as a function of biasing conditions. Figure 6 shows the optical gap plotted as a function of energy flux. The optical gap was determined from the Tauc plot of the absorption coefficient using a linear extrapolation of the absorption edge[6]. The figure shows the optical gap decreasing rapidly initially, as a function of ion energy flux, and then leveling off, again at an energy flux of about 4 mJ $cm^{-2}s^{-1}$.

Concurrent with the decrease of the optical gap, we also found that the Urback edge[7] (the optical absorption associated with localized states near the band edges) became less and less distinctive. The localized states are presumed to be at least partly associated with an incomplete three dimensional amorphous network, so the above trend is consistent with the rapid decrease of $-CH_3$ group concentration as demonstrated in figure 5. The localized states can also serve as effective fluorescence centers in the a-C:H films[8]. In fact, a strong fluorescence background prevented the acquisition of Raman spectra for films produced with an energy flux less than 2.3 mJ $cm^{-2}s^{-1}$. Other films grown under higher energy flux, however, have shown Raman spectra characteristic of the amorphous carbon phase.

4 DISCUSSION

The experimental results described above suggest that there are close correlations among various film properties. In the region of relatively low ion energy flux, the supplied energy seems to act to promote crosslinking between carbon chains to expand the three dimensional amorphous network. This is indicated by the rapid decrease in both methylene and methyl group concentrations as a function of ion energy flux in the region of relatively low flux. The structural network is not built up only with the sp^3 bonding configuration, but is inevitably accompanied by the formation of sp^2 clusters or π bonded domains, which account for the decrease of the optical gap[9], as seen in figure 6. The presence of small domains of graphite-like structure at the surface of a-C:H films has also been observed by scanning tunneling microscopy[10,11] The expansion of the three dimensional network also results in a significant increase in hardness. However, in this region of relatively low ion energy flux, the films likely still maintain some degree of deformability, resulting in a relief of any compressive stress which might build up. As a result, the compressive stress remains below our limit of detection up to a hardness of 8GPa and an ion energy flux of 4 mJ $cm^{-2}s^{-1}$.

In the ion energy flux range greater than about 4 mJ $cm^{-2}s^{-1}$, almost no change in methylene group concentration or optical gap is seen, and the methyl group concentration falls close to zero. Nevertheless, the hardness continues to increase considerably, from about 15 GPa up to more than 30 GPa. Since the crosslinking seems to have been mostly completed already at lower energy flux values, the factor remaining which could account for the hardening is a densification of the films. In fact, the density of the film grown on the pulsed biased electrode with a flux of about 4 mJ $cm^{-2}s^{-1}$, was approximately 1.4 g/cm^3, still less than that of films produced on the rf powered electrode (approx. 1.7 g/cm^3). The deformability of the material is probably less at these high ion energy flux values, so the compressive stress now begins to increase in parallel with the hardness.

This work demonstrates how the various changes in film properties relate to each other, and to the plasma conditions. The control of these properties is

important for practical applications. The results have shown how the control of ion energy flux can give one control over various film properties.

5 ACKNOWLEDGEMENTS

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7 List of Figures

Figure 1. Schematic diagram of the Faraday cup system used to measure the total ion flux.

Figure 2. Oscilloscope trace of the measured current under pulsed biasing conditions. The equivalent shape of the background level and the total current level, measured with the ion orifice open, indicates that no measurable temporal variation in ion current exists.

Figure 3. Apparent ion flux on the substrate for various deposition conditions.

Figure 4. The upper plot shows the a-C:H deposition rate as a function of ion energy flux. In the lower plot, the hardness and compressive stress of the a-C:H films is plotted vs. ion energy flux. While the deposition rate is independent of ion energy flux, the hardness and compressive stress of the films increase smoothly with increasing ion energy flux.

Figure 5. Concentrations of methylene ($-CH_2-$) and methyl ($-CH_3$) groups in the films as a function of ion energy flux. At an energy flux of approx. 4mJ cm^{-2} s^{-1}, the methyl concentration has dropped close to zero and the methylene concentration begins to plateau at a finite value.

Figure 6. Changes in the optical gap of a-C:H films as a function of ion energy flux. The optical gap decreases rapidly with increasing ion energy flux initially, and then begins to level off. The decrease is likely the result of the presence of π bonded domains, formed in the films as a result of ion bombardment.

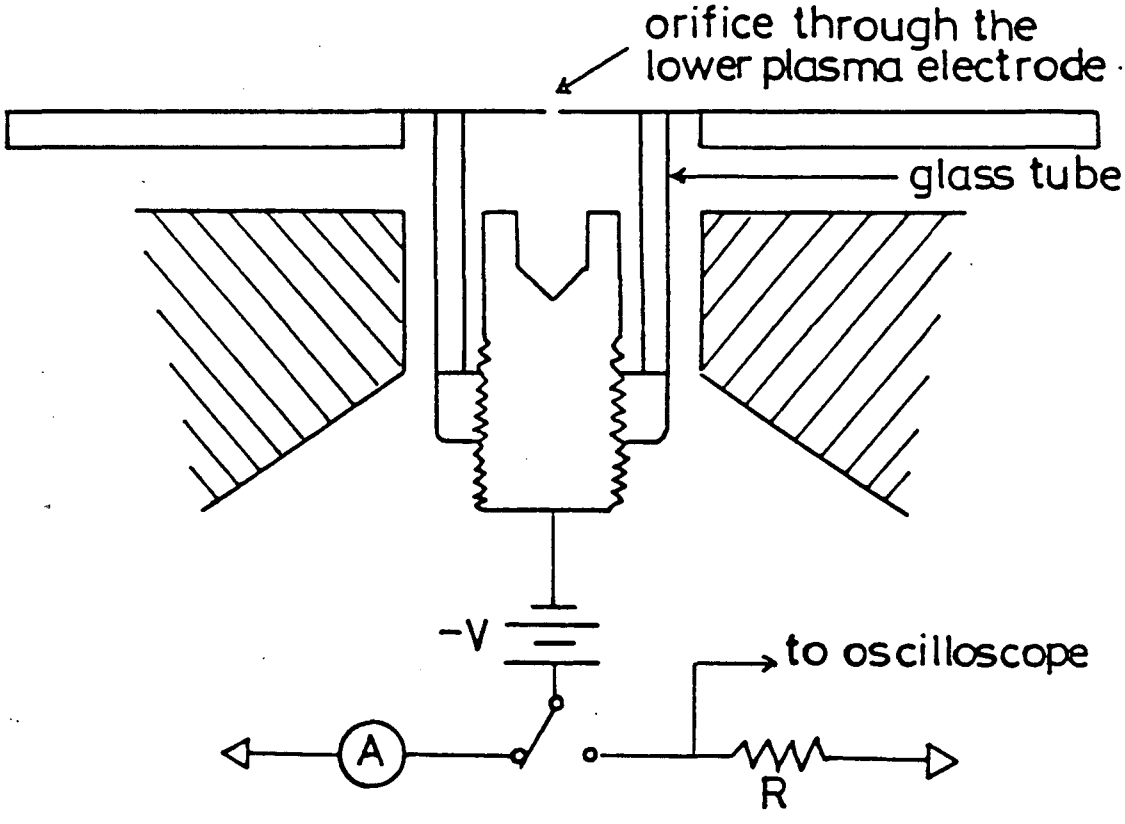

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Figure 1

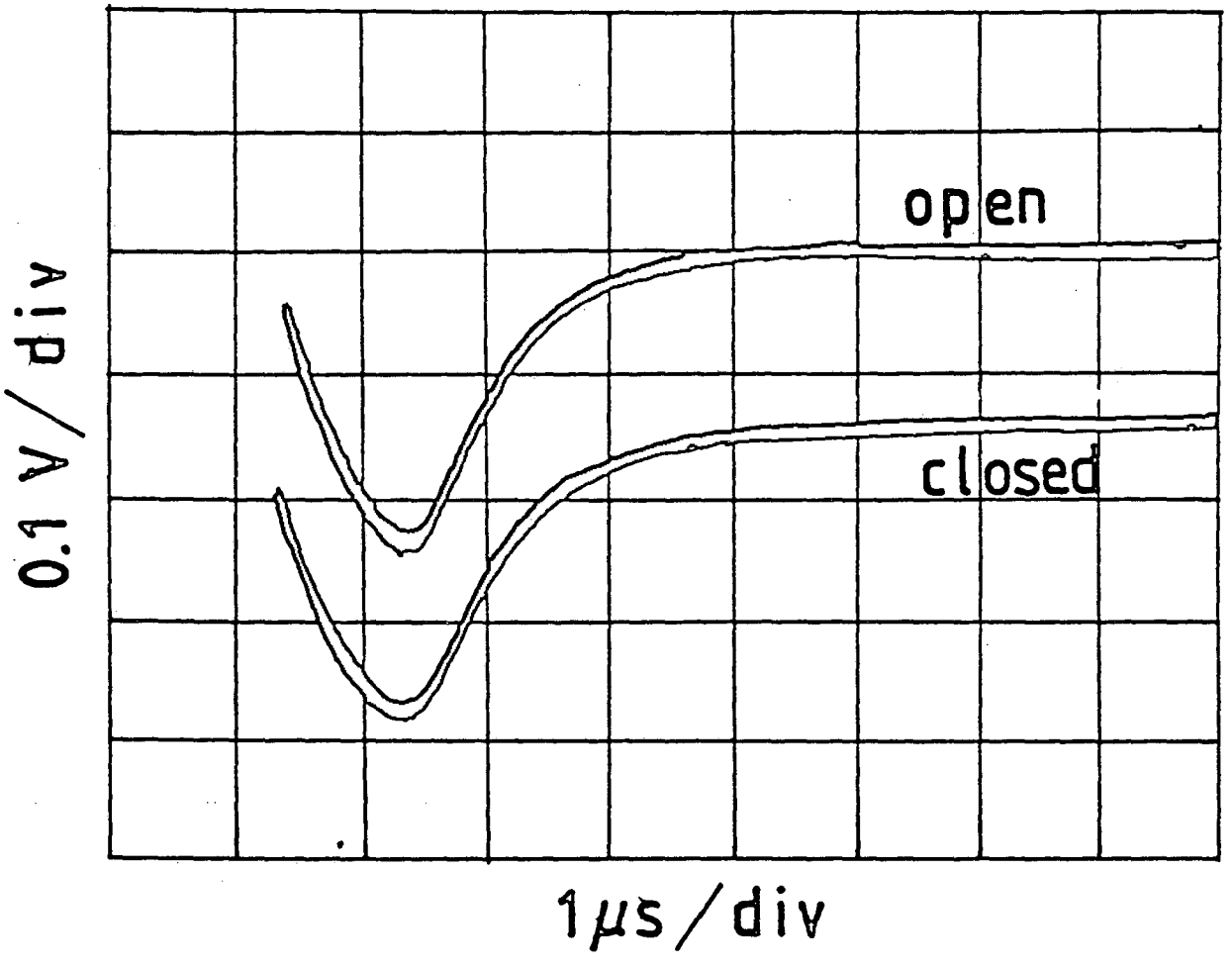

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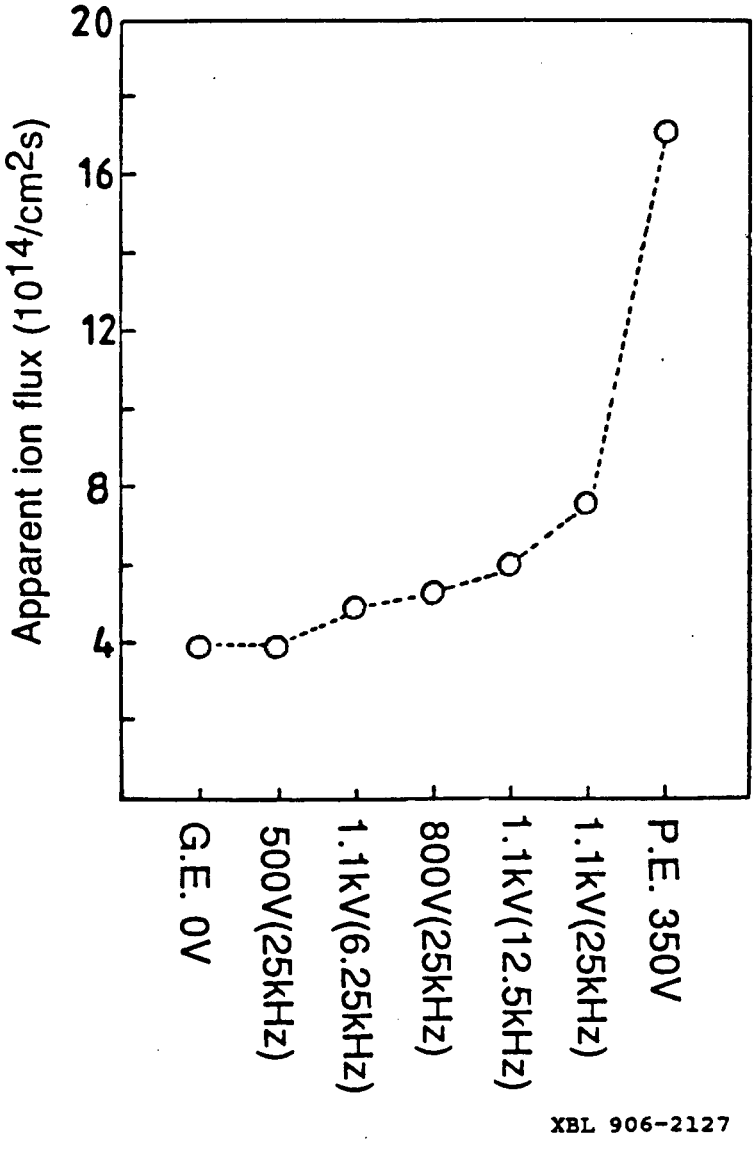
Figure 2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20
16
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Apparent ion flux (10^{14}/cm^{2}s)
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Figure 3

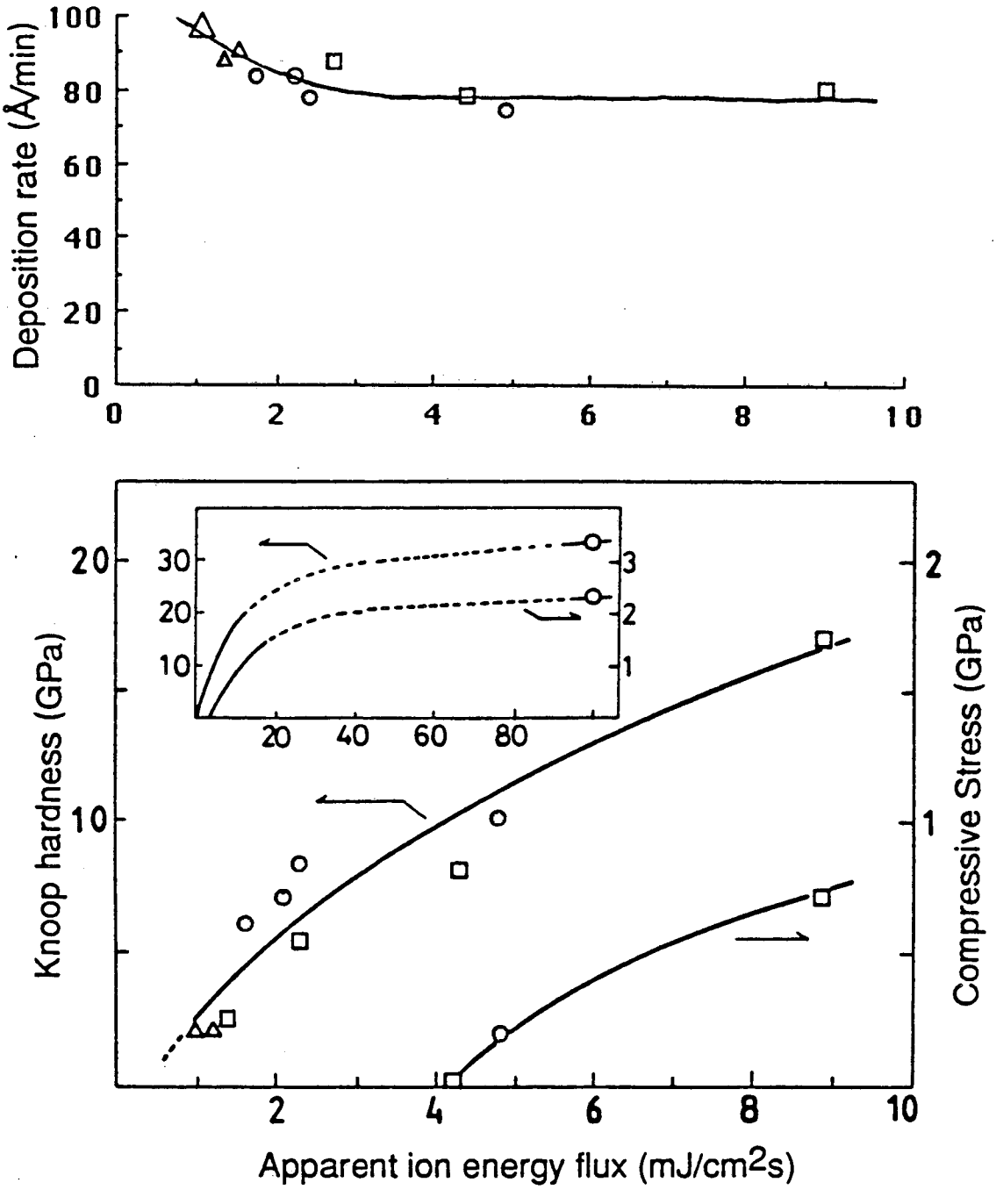

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Figure 4

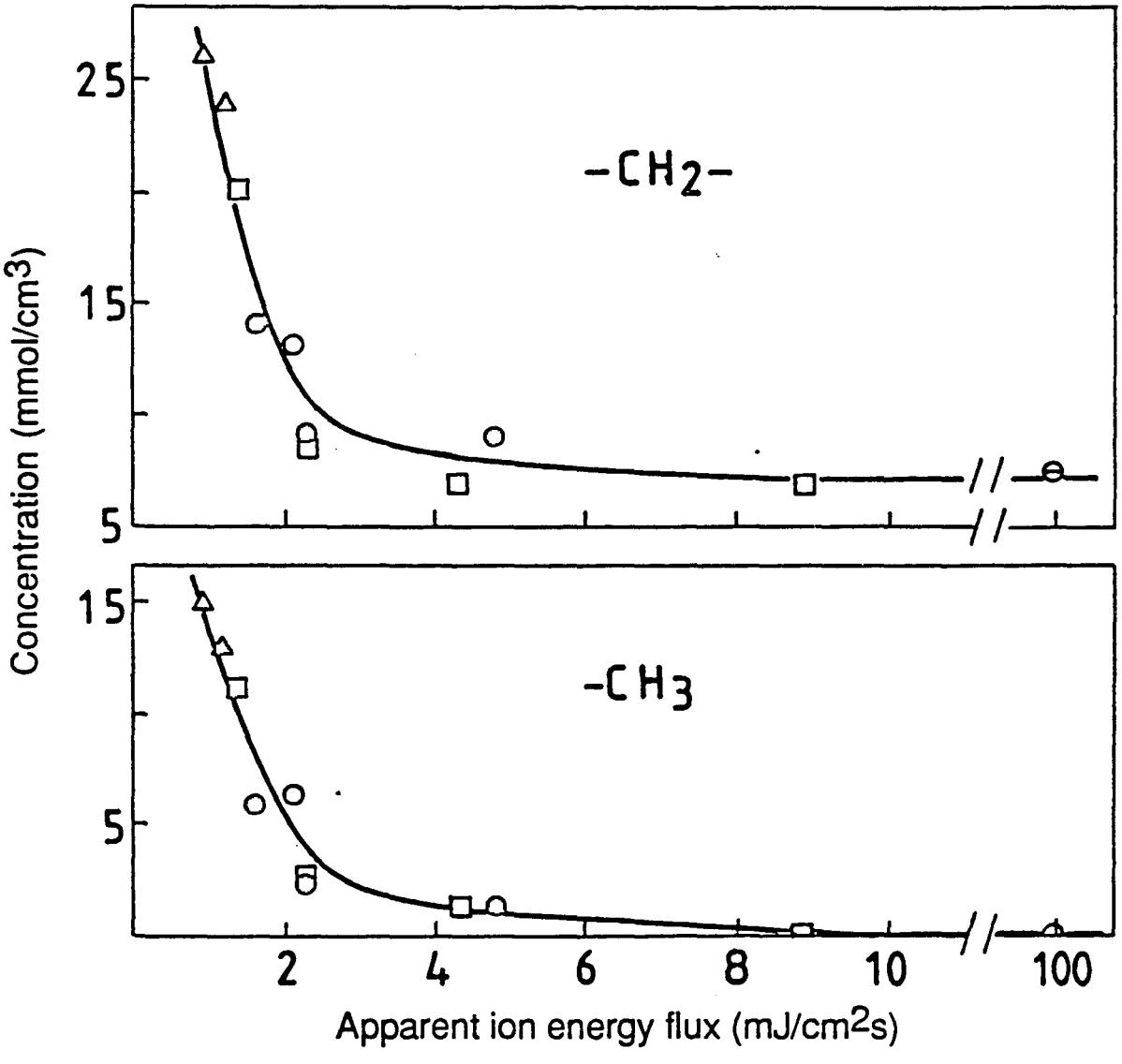

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Figure 5

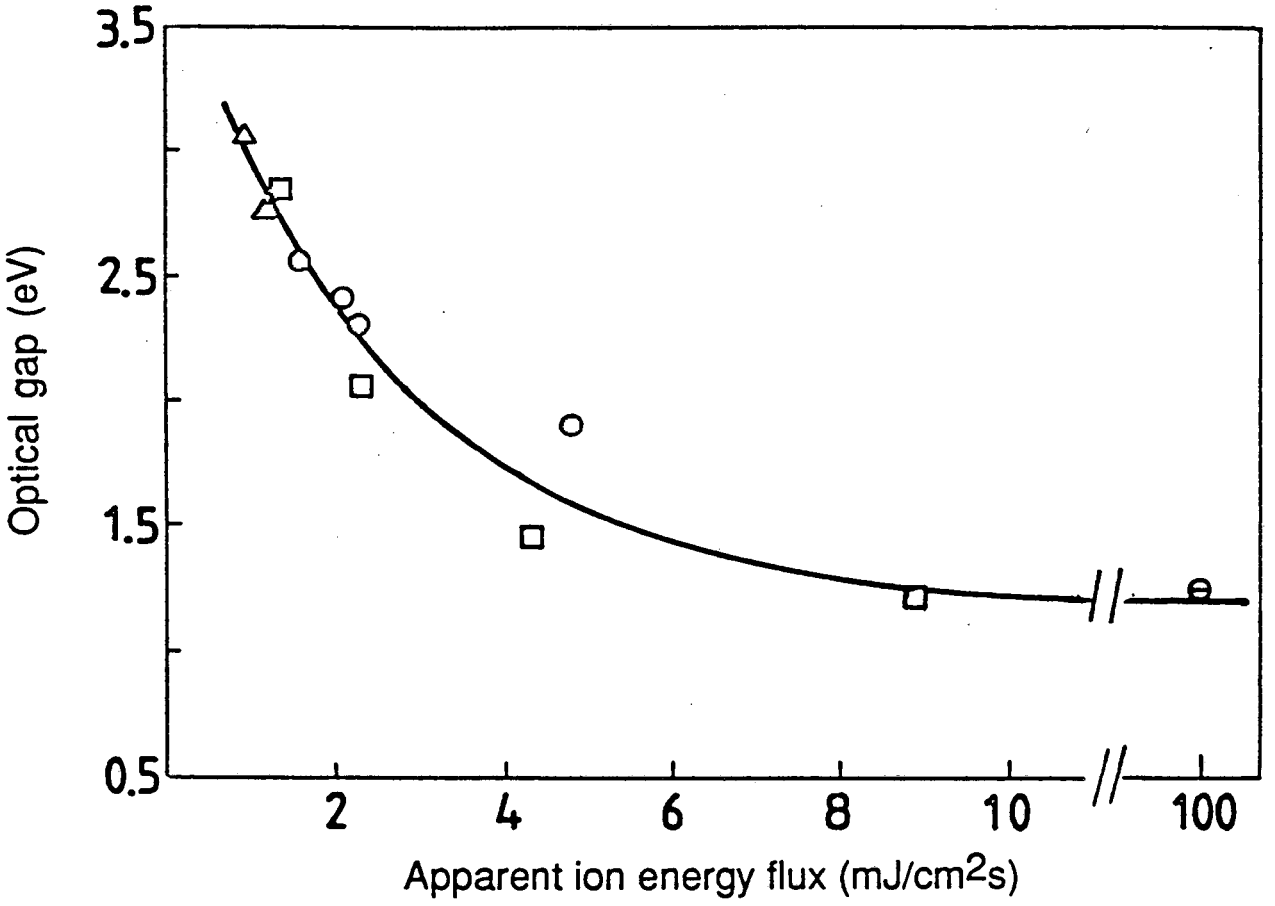

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Figure 6

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