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LASER DAMAGE OF DIAMOND FILM WINDOWS

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The many unique physical properties of diamond make it useful as a thin film coating for laser optics. We have calculated the laser induced thermal stress resistance for diamond and other optical materials. The calculated stress resistance for diamond is orders of magnitude higher than any other material and, therefore, diamond films should have a higher laser damage threshold. Calculations also indicate that diamond film, because of its high thermal conductivity, exhibits tolerance for isolated impurity inclusions. Polycrystalline diamond films were deposited on silicon substrates using a d.c. plasma enhanced chemical vapor deposition process. The films were characterized by Raman and optical absorption spectroscopy and by ellipsometry. Laser induced damage thresholds of diamond film windows and films on silicon substrates were measured for single pulses of 532 nm and 1064 nm laser radiation. The measured damage thresholds for diamond windows are 6.0 J/sq.cm (300 MW/sq.cm) at 532 nm and 12.4 J/sq.cm (620 MW/sq.cm) at 1064 nm. For diamond on silicon, the damage thresholds are 3.65 J/sq.cm (182 MW/sq.cm) at 532 nm and 14.4 J/sq.cm (720 MW/sq.cm) at 1064 nm. These values compare favourably with those for other common materials used as optical coatings.

1. INTRODUCTION

Diamond has many unique properties distinguishing it from other solid state materials. Its thermal, mechanical and optical properties are superior to those of other widely used semiconductors. Many important properties of diamond are shown in Table 1 and compared with those of other group IV elemental semiconductors and gallium arsenide. As is evident, the thermal conductivity, hardness and breakdown field are several times higher than the other materials listed, suggesting resistance to damage from intense optical radiation. These properties of diamond have already been effectively exploited to develop electrical and optical devices.[1-3] The wide bandgap and stable color centers in diamond have also been used to make tunable solid state lasers.[4] However, the lack of large scale economical production of high quality films has limited wide spread application of diamond films.

Chemical vapor deposition of diamond films using reactive pulse plasma, hot filament, electron bombardment and d.c. plasma have been reported.[5-11] With the progress achieved in chemical vapor deposition of diamond films, new applications of diamond films in laser optics are possible. Since surfaces of optical elements are often most sensitive to laser damage, increasing the surface damage threshold with an optical coating can be expected to improve the damage threshold of these elements. High reflection and anti-reflection coatings on optical elements in laser systems are used to optimize

Table 1
Comparison of important properties of diamond with other semiconductors

Properties	Ge	Si	GaAs	Diamond
Band Gap (eV)	0.66	1.12	1.43	5.45
Breakdown Field (V/cm)	$\sim 10^5$	5×10^6	6×10^6	$>10^7$
Carrier Lifetime (s)	2×10^{-4}	2.5×10^{-3}	10^{-8}	$\sim 10^{-10}$
Dielectric Constant	16	11.8	13.1	5.5
Electron Mobility (cm^2/V-s)	3900	1500	8500	1900
Electron Velocity (cm/sec)	6×10^6	1×10^7	2×10^7	2.7×10^7
Hardness (Kg/mm^2)	780	10^3	600	10^4
Hole Mobility (cm^2/V-sec)	1900	600	400	1600
Lattice Constant (A^o)	5.64	5.43	5.65	3.57
Melting Point (^oC)	941	1420	1238	~3800
Refractive Index	5.6	3.4	3.6	2.4
Resistivity (Ohm-cm)	43	2.5×10^5	4×10^8	$>10^{16}$
Thermal Cond.(W/cm-^oK)	0.64	1.45	0.46	20
Thermal Expansion Coeff.	5.5×10^{-6}	2.6×10^{-6}	5.9×10^{-6}	8×10^{-5}

performance. These films most often are the weak elements which limit the energy flux from a laser. Improvements in the laser damage threshold, E_d, of these films will significantly reduce design requirements as well as increase the transmitted laser power limits. Conversion efficiency of nonlinear crystals such as KDP or KTP increases with input power but the low damage threshold of these crystals prevent their optimum use. If damage threshold can be increased by coating the crystals with appropriate films then higher conversion efficiencies can be obtained.

2. THERMAL STRESS RESISTANCE PARAMETER

One measure of the laser damage tolerance of a material is the laser induced thermal stress resistance parameter, R_T, defined by the following expression,

$$R_T = \sigma_f K(1-v)/\alpha E \qquad (1)$$

where σ_f is the tensile fracture strength, K is the thermal conductivity, v is Poisson's ratio, α is the thermal expansion coefficient and E is the elastic modulus. R_T has been used as a figure of merit for evaluating laser materials tolerance to laser damage.[12] The higher the thermal stress resistance parameter of a material, the higher its laser damage threshold. We have calculated R_T for diamond as well as other common laser materials; the results are shown in Fig. 1 as a plot of log K versus log R_T.

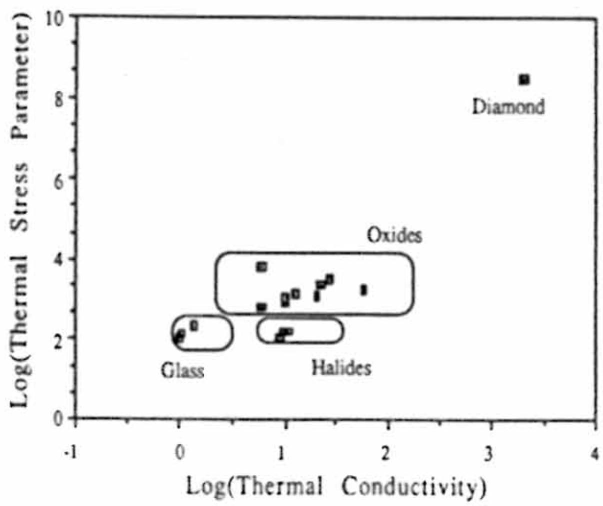


Figure 1. Thermal Condutivity, K versus Thermal Stress Parameter, R_T.

The thermal conductivity and thermal stress resistance of similar materials cluster together in groups. The oxide group includes sapphire, spinel and commonly used garnets (YAG, GSGG). The halide group includes fluorides and chlorides of magnesium, calcium and lithium and the glass group includes phosphate and silicate glass. Diamond, having a thermal conductivity several times higher and a thermal stress parameter orders of magnitude higher than the other laser materials, appears to be a good choice as a material tolerant to laser damage. Diamond films may be used for a variety of optical coatings as well as for optical windows. Therefore, it is important to measure the laser damage threshold of diamond films.

3. LASER INDUCED DAMAGE

3.1 Dielectric Breakdown

If the damage is due to dielectric breakdown induced by the laser radiation, the laser power density, P_d, is related to the dielectric breakdown field, V_b, by the equation,

$$P_d = V_b^2 \, n/Z_o \qquad (2)$$

where n is the refractive index and Z_o is the impedance of free space. For bulk diamond, Equation (2) gives P_d = 600 GW/cm^2. For 10.6 µm laser radiation a threshold of 4 GW/cm^2 has been measured for bulk diamond.[13] In the case of thin films of high bandgap materials, the Forlani-Minnaja law[14] predicts $V_b \propto d^{-1/2}$ where d is the film thickness. Therefore, diamond thin films should have a high breakdown field and a high laser damage threshold.

3.2 Damage due to Impurities

When the films contain impurities and inclusions which absorb the laser radiation the damage is caused by the thermal stress induced by laser heating. The temperature rise of the host due to a spherical impurity absorbing radiation as shown in Fig. 2 is given by[15,16]

$$T_p = \frac{a^2 QI}{K_p}\left[\frac{1}{3}\frac{K_p}{K_h} + \frac{1}{6}\left(1 - \frac{r^2}{a^2}\right) - \frac{2ab}{r\pi}\int_0^{\infty} \frac{e^{-\frac{y^2 t_p}{\gamma_1}}}{y^2} \frac{(\sin y - y\cos y)(\sin(ry/a))\, dy}{(c\sin y - y\cos y) + b^2 y^2 \sin^2 y}\right]$$

K_p and K_h are the thermal conductivity of the impurity and host respectively, a is the radius of the impurity, Q is the absorption cross section, I is the laser intensity, t_p is the laser pulse duration and $b = [(K_p{}^2 D_h)/(K_h{}^2 D_p)]^{1/2}$. $c = 1-(K_h/K_p)$ and $\gamma_1 = a^2/D_p$, where D_p and D_h are the thermal diffusivity of the impurity and the host. The above equation can be solved for the laser energy required for the melting points of the impurity or the host.

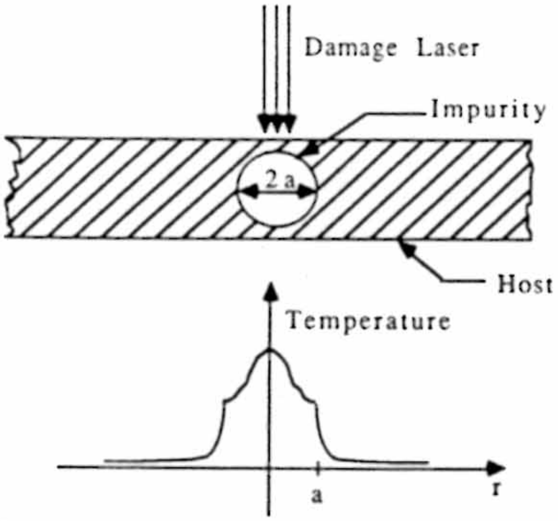


Figure 2. Schematic of laser absorption and temperature rise in a host containing an isolated impurity

In Fig. 3 we show the variation of threshold energy density, required for breakdown at a = r, with K_h when various isolated impurities are present in the host. It is clear that the damage threshold of diamond is not severly affected by the impurities. Also for r>>a, the calculated value of E_d for diamond film was found to be a constant, independent of the thermal conductivity of the impurities.

4. EXPERIMENT

The diamond films were prepared by a plasma enhanced chemical vapor deposition (PECVD) process. Typical range of conditions employed were as follows:

Temperature:	600 to 800^oC
Pressure:	20 to 30 Torr
CH_4/H_2:	0.1 to 5

Silicon wafers were used as substrates. Free-standing diamond film windows were produced by etching back the substrate. Laser damage on the samples was induced by varying the energy from 1 to 100 mJ from a 1064 nm Nd:YAG laser with a pulse duration of 20 ns. Silicon, diamond film on silicon and diamond film

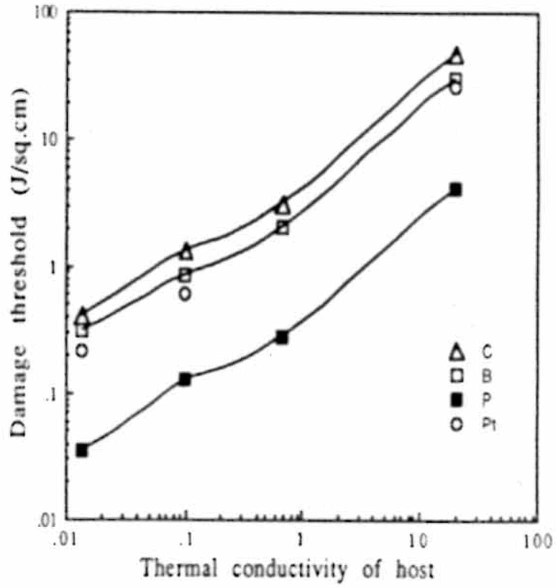


Figure 3. Variation of damage threshold with thermal conductivity of hosts containing impurities.

windows were used as samples. The diameter of the laser spot at the impact point was measured using an array detector. The laser damage threshold was measured using the setup shown schematically in Fig. 4. The sample was mounted on an X-Y-Z microposition stage. A He-Ne laser was used as a probe to measure the reflectance of the surface.

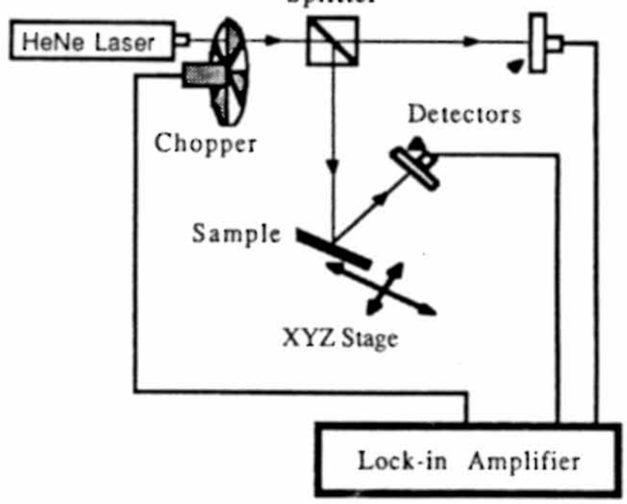
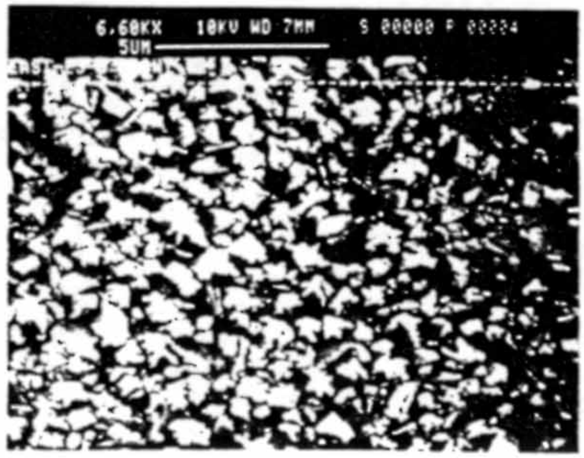


Figure 4. Schematic diagram of the differential reflectometer used in the damage threshold measurements.

The reflection from an undamaged portion of the surface was detected and fed to the lock-in amplifier along with the reference signal to obtain a null point. The probe was then positioned on the damaged spot and the intensity of the reflected beam was measured. A deviation from the null condition occurred when the reflected intensity changed, due to absorption and scattering from the damaged spot. The deviation was measured as a function of laser damage energy. The damage on the films was also confirmed by using a low power optical microscope. The experimental set-up could be easily modified to detect the scattered light by blocking the specular reflection. The refractive index of the film was measured using an ellipsometer and the films were analyzed using Raman and absorption spectroscopy and scanning electron microscopy.

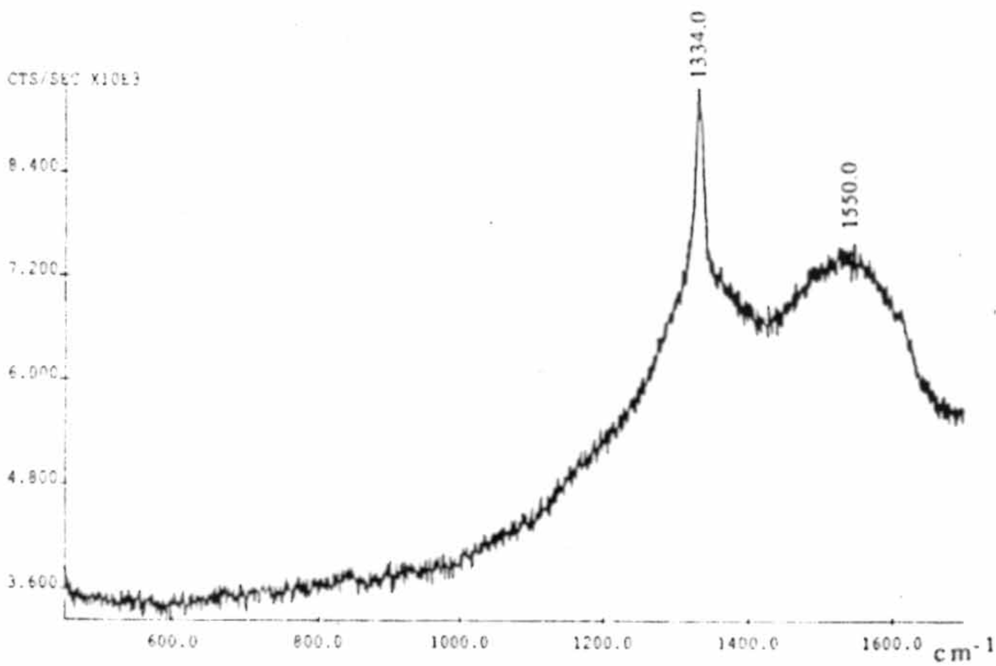
5. RESULTS AND DISCUSSION

All the diamond film samples studied were polycrystalline. The front surface was faceted whereas the back surface (etched-back) was smoother than the front as shown in the SEM photograph (Fig. 5a & b). The corresponding Raman spectra of these surfaces are shown in Fig. 5c & d , however, there is no significant differences between the spectra from the front and back surfaces of the film. All the diamond films showed characteristic first order Raman spectral line around 1332 cm^{-1}, which may be compared with the spectrum shown in Fig. 5e for a natural bulk diamond. The significant

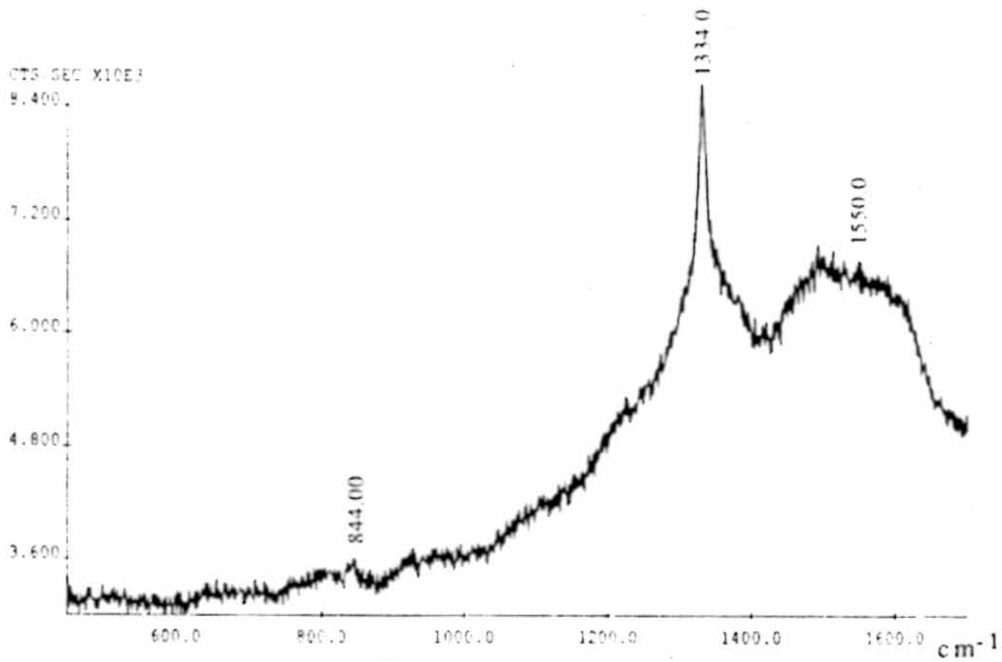


(a)

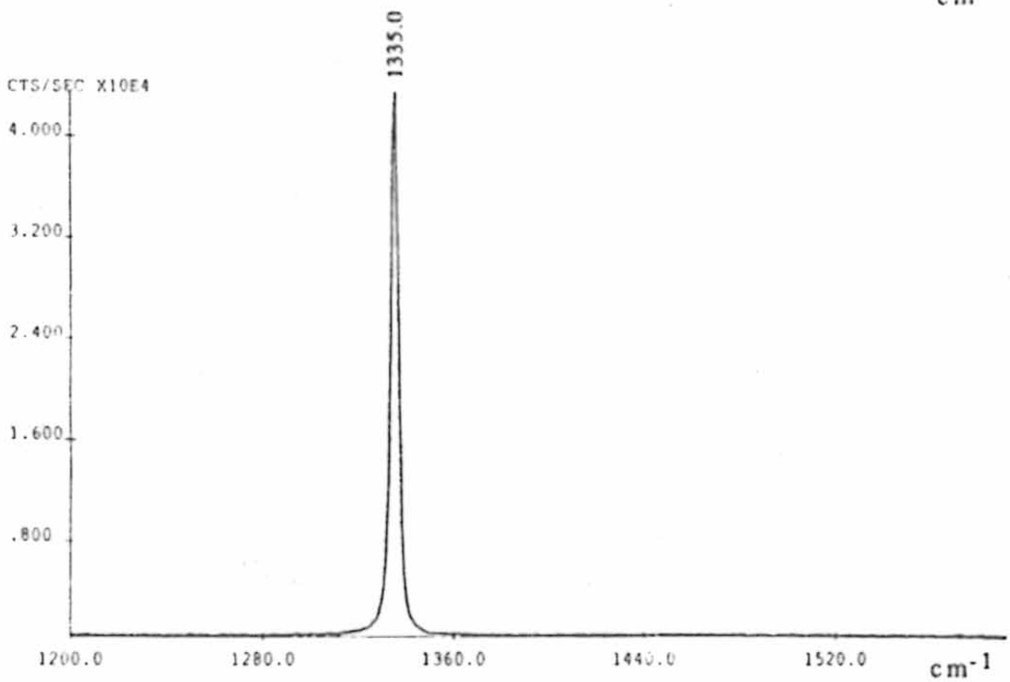
(b)



(c)



(d)



(e)

Figure 5. (a) and (b) SEM of the front and back of a diamond film window, (c) and (d) corresponding Raman spectra and (e) a Raman spectrum of a bulk diamond sample.

difference between the spectra is a broad fluorescence background centered around 1550 cm^{-1} for the diamond film, which is an indication of the presence of sp^2 bonding due to graphitic carbon in diamond film. The refractive index of various samples, measured using ellipsometry, was in the range of 2.6 to 2.7 which is higher than the bulk value of 2.41. This is probably due to graphitic inclusions in the film and also due to surface roughness.

The absorbance spectrum of diamond films was measured using a Perkin Elmer spectrophotometer and is displayed in Fig. 6, for the wavelength range from 500 to 1500 nm. Interference effects due to the film (1.87 μm) can be clearly seen. No correction for Fresnel reflectance from the film has been made in the absorbance spectrum shown. Absorption of the film increases towards shorter wavelengths. The absorption coefficients derived from Fig. 6 by applying the corrections for reflectance are $\alpha_{532} = 3.93 \times 10^3\ cm^{-1}$ and $\alpha_{1064} = 1.20 \times 10^3\ cm^{-1}$.

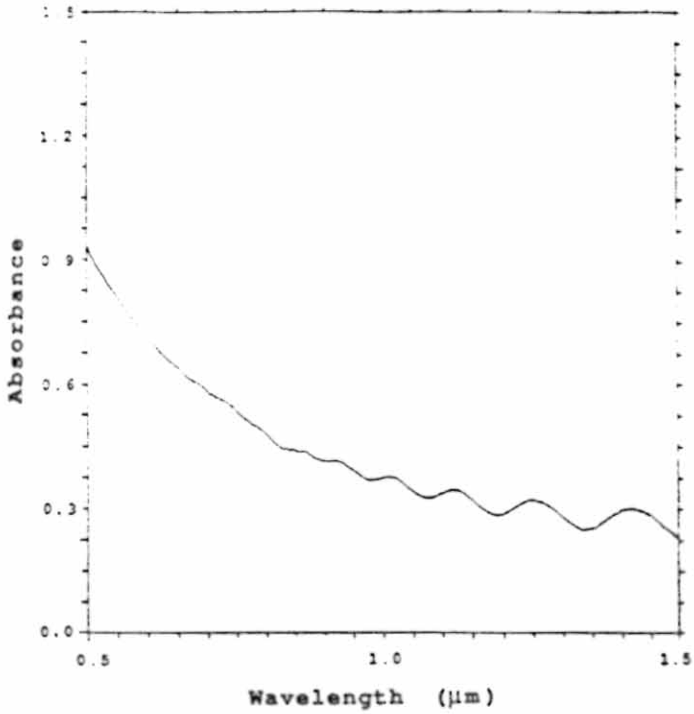


Figure 6. Absorbance spectrum of 1.87 μm diamond film.

In Fig. 7a and b we show the results of laser damage on silicon substrate, diamond film on silicon and diamond film windows for 532 and 1064 nm laser radiation respectively. The output signal from the lock-in amplifier is plotted against the laser energy. The damage threshold of silicon was measured to be 5.3 J/cm^2 (265 MW/cm^2) for 1064 nm and 2.1 J/cm^2 (105 MW/cm^2) for 532 nm laser pulses. These are within the range of values reported for silicon.[13] The irradiated spots were also examined using a low power optical microscope for laser indced damage and the threshold energy agreed with that determined by the reflectance technique. The absorption coefficients of silicon at these wavelengths are high and energy transfer by resonant surface plasmons has been considered as a damage mechanism.[17] The measured damage thresholds for a silicon substrate coated with a 1.87 μm diamond film are 3.65 J/cm^2 (182 MW/cm^2) at 532 nm and14.4 J/cm^2 (720 MW/cm^2) at 1064 nm. The reflectance of silicon substrate is about 30% and the 1.87 μm diamond film corresponds to approximately an equivalent optical thickness of quarter wavelength at 532 nm. For this

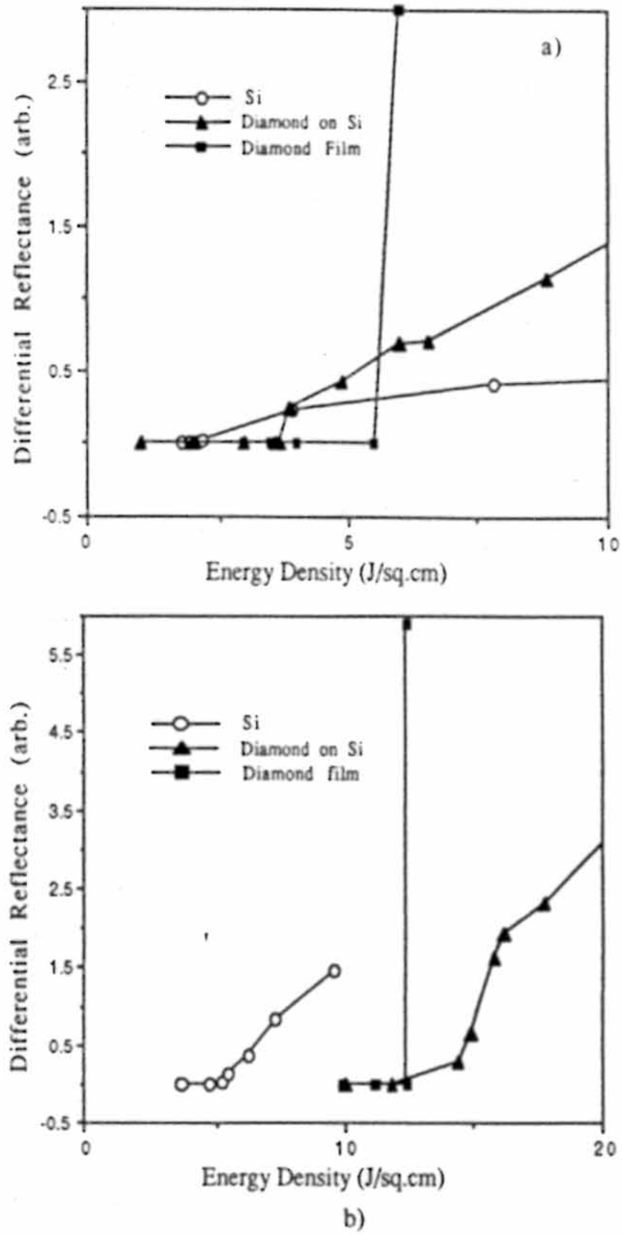


Figure 7. Differential reflectance as a function of laser energy density of (a) 532 nm and (b) 1064 nm.

film-substrate combination, the reflectance is reduced to approximately 8%. Assuming the laser damage threshold of diamond to be higher than silicon, it is reasonable to expect a threshold of 1.6 J/cm^2 for this film-substrate combination, if the damage occurs mainly at the substrate. The measured damage threshold at 532 nm is higher than that of the substrate, showing the effectiveness of a diamond film for laser hardening. In the case of 1064 nm laser radiation, the same diamond film has an optical thickness of non-quarter wavelength; hence the reflectance of the film-substrate combination is between 8 and 30%. Morever, for a non-quarter wavelength film the maximum electric field due to the laser radiation will be within the film rather than at the interface. Such a design has been shown to be beneficial in achieving a high damage threshold for optical coatings.[18] The high damage threshold of 14.4 J/cm^2 at 1064 nm obtained for the film-substrate combination is an indication that diamond film will be useful for a variety of optical coating applications involvng high power lasers.

For a diamond film thickness of 1.87μm, the laser damage thresholds at 532 and 1064 nm were found to be 6.0 J/cm^2 (300 MW/cm^2) and 12.4 J/cm^2 (620 MW/cm^2) respectively. These values are substantially higher than those measured for the silicon substrate. Thus, the low damage threshold of the film-substrate combination discussed above for 532 nm is not due to the diamond film. However, the damage threshold measured for free-standing diamond film is lower than theoretically predicted value. Since the films have high absorption coefficient due to sp^2 bonded carbon the contribution from these impurities will be substantial in determining the damage threshold. However, the damage threshold may be further improved by optimizing deposition conditions.

In Fig. 8 we show the SEM photographs of laser damage. There is an obvious difference in the nature of damage on silicon substrate and on film-substrate combination. Surface melting is visible on silicon whereas the damage on the latter appears to be due to dielectric breakdown. The diamond films developed cracks during laser damage suggesting that the film stress may influence the damage threshold.

6. SUMMARY

Free-standing diamond films have a high laser damage threshold at 532 and 1064 nm; therefore they are useful as laser windows and as an overcoat for high reflectors and undercoat for antireflectors. In combination with suitable substrates, diamond films can be an excellent antireflection coating for infrared windows. However, the experimentally measured damage threshold was found to be lower than the calculated values. Dielectric breakdown induced by the laser raaiation seems to be responsible for the damage in diamond films, though the thermal stress induced by highly absorbing sp^2 bonded carbon impurities may be a contributory factor. Deposition conditions as well as stress of the film may influence the damage threshold.

(a)

(b)

(c)

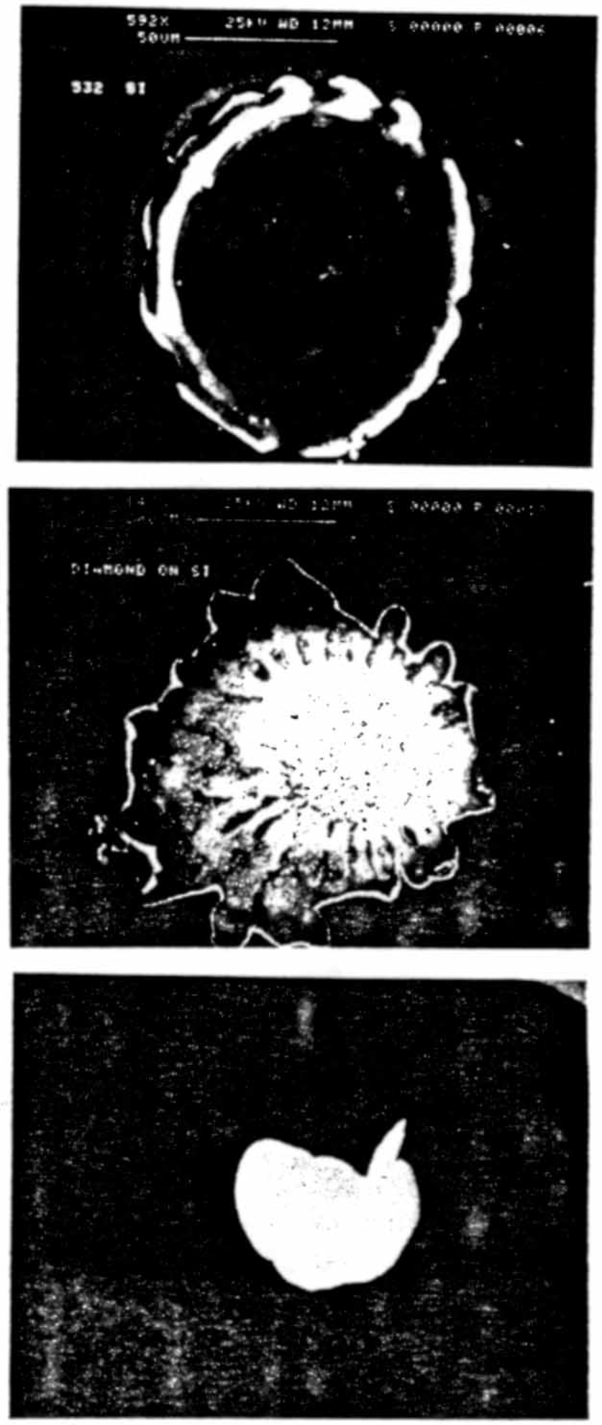


Figure 8. Micrographs of laser damage on (a) Silicon, (b) diamond film on Silicon and (c) diamond film window.

7. ACKNOWLEDGEMENT

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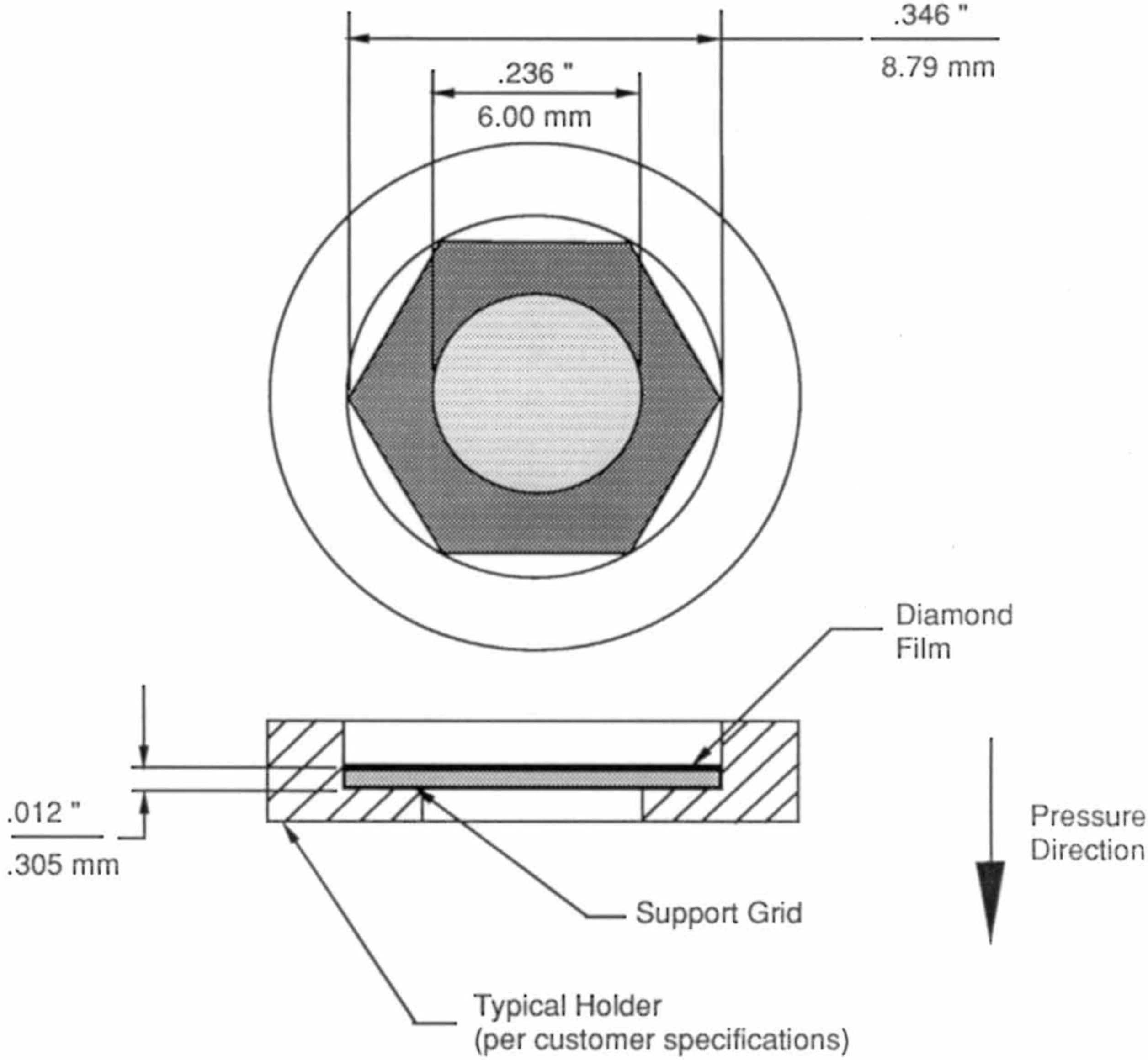
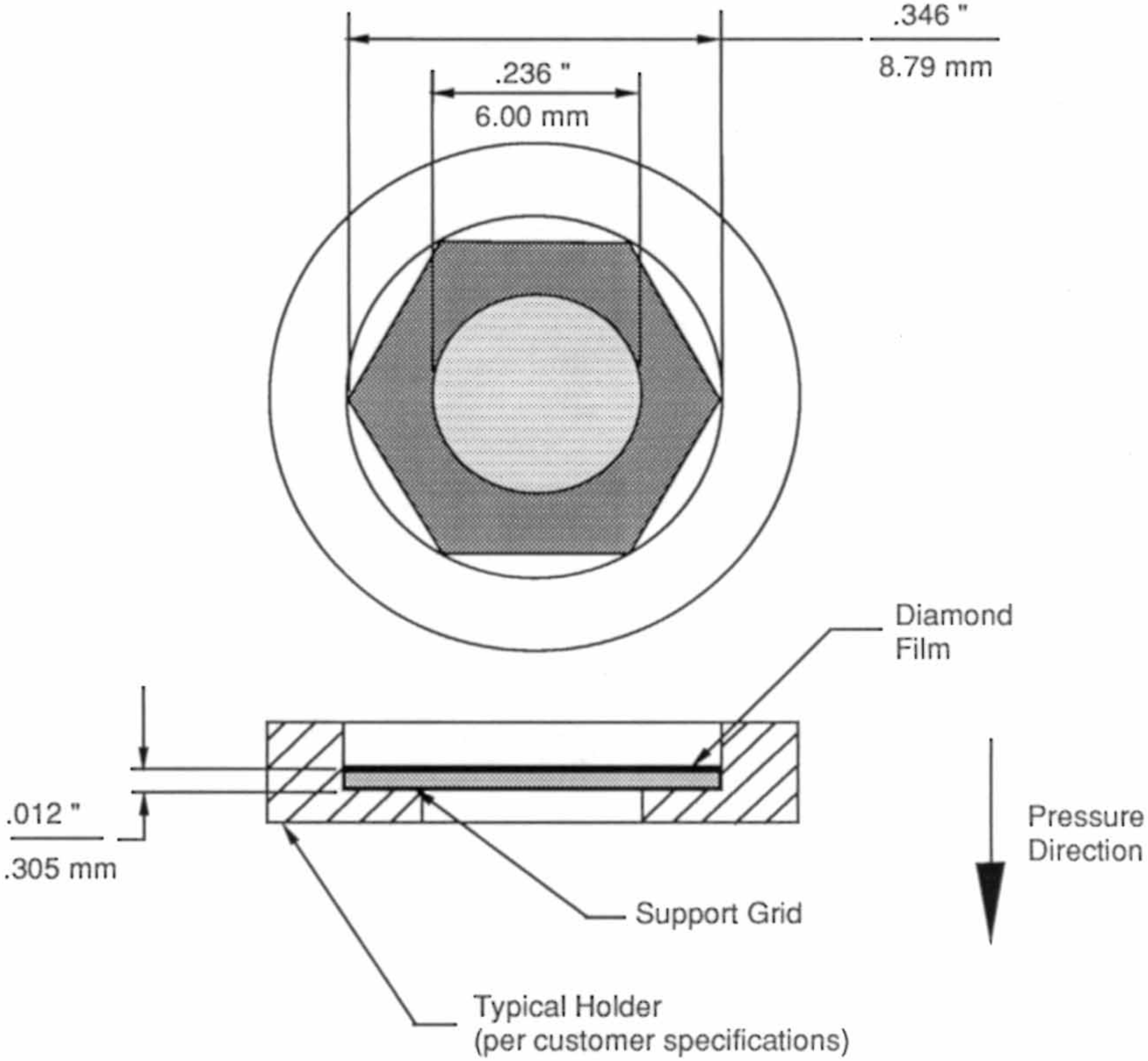


Specifications:

(1) Aperture Dia:	6 mm
(2) Support Grid Dia:	8.8 mm O.D.
(3) Transmission of Support Grid:	70 %
(4) Thickness of Support Grid:	0.3 mm
(5) Pressure Rating:	1.25 atm(1.0 atm operation)
(6) Pressure Cycling:	5000 + cycles; 1 atm
(7) Leak Rate (He):	< 1 X 10(-9) atm cc / sec

Diamond X-Ray Window



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