Diamond films for laser hardening

S. Albin and L. Watkins
Department of Electrical and Computer Engineering, Old Dominion University, Norfolk, Virginia 23529
K. Ravi and S. Yokota
Crystallume, 125 Constitution Drive, Menlo Park, California 94025

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Diamond has many unique physical properties useful as thin-film coatings for laser optics. The calculated value of the laser-induced stress resistance parameter of diamond is orders of magnitude higher than any other material and, therefore, diamond films should have a higher laser damage threshold. This is confirmed by laser damage experiments carried out on free-standing polycrystalline diamond films. Materials susceptible to laser damage can be protected by diamond thin-film coatings to enhance the damage threshold. This is demonstrated in the case of diamond coated silicon substrate.

Diamond has many unique physical properties which are technologically important. Its thermal conductivity, hardness, and breakdown field are several times higher than those of other solid-state materials. These properties of diamond have already been effectively exploited to develop electrical and optical devices.[1-3] The wide band gap and stable color centers in diamond have also been used to make tunable solid-state lasers.[4] These properties also lead to resistance to damage from intense optical radiation. 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 antireflection coatings on optical elements in laser systems are used to optimize performance. These films most often suffer from laser damage at low threshold which limits the energy flux from a laser. Improvements in the laser damage threshold of these films will significantly reduce design requirements as well as increase the transmitted laser power limits. Conversion efficiency of nonlinear crystals increases with input power, but the low damage threshold of such crystals prevents their optimum use. If damage threshold can be increased by coating the crystals with appropriate films, then higher conversion efficiencies can be obtained; diamond film can be one of such coatings.

One measure of the laser damage tolerance of a material is the laser-induced thermal stress resistance parameter R_T, which depends on the tensile fracture strength, thermal conductivity, Poisson's ratio, thermal expansion coefficient, and elastic modulus. R_T has been used as a figure of merit for evaluating laser material tolerance to laser damage.[5] It is found that the higher the R_T value of a material, the higher its laser damage threshold. We have calculated R_T for diamond as well as other common materials; the results are shown in Table I. Diamond, having a thermal conductivity several times higher and a thermal stress parameter orders of magnitude higher than the other materials, appears to be a good choice as a material tolerant to laser damage. Hence diamond films may also be useful for a variety of optical coatings as well as for optical windows. Therefore, it is important to study the laser damage threshold of diamond films and its effectiveness as a coating for laser hardening of materials having low damage threshold.

Chemical vapor deposition of diamond films using reactive pulse plasma, hot filament, electron bombardment, and dc plasma has been reported.[6-12] With the progress achieved in chemical vapor deposition of diamond films, new applications of diamond films in laser optics are possible. For the results reported here the diamond films were prepared by a plasma-enhanced chemical vapor deposition (PECVD) process. Typical ranges of conditions employed were as follows:

Temperature	600–800 °C
Pressure	20–30 Torr
CH4/H2	0.1–5

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. The beam profile and the diameter of the laser spot at the impact point were measured using a scanned array detector. The laser damage threshold was measured using a differential reflectometer setup shown in Fig. 1. 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. 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 high-energy laser beam was incident at this spot, and the intensity of the reflected probe beam was measured. A deviation from the null condition occurred when the reflected intensity changed, due to absorption and scat-

TABLE I. Comparison of thermal conductivity and thermal stress resistance parameter of diamond with other materials.

Material	Thermal conductivity (W/m K)	R_T (W/m)
Diamond	2000	3.0×10^{8}
Silicon	1.5	2.0×10^{4}
Silver	406	1.8×10^{4}
Sapphire	28	3.4×10^{3}
Magnesium fluoride	21	1.3×10^{3}
Glass	0.62	7.0×10^{1}

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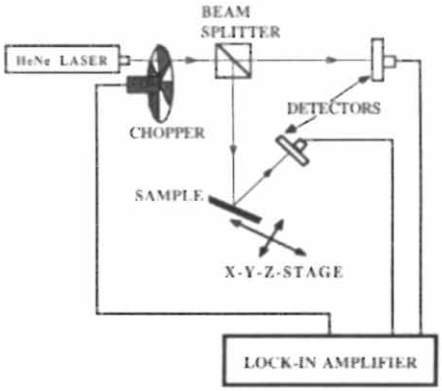

FIG. 1. Schematic diagram of the differential reflectometer for damage threshold measurement.

tering 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 films were analyzed using Raman and absorption spectroscopy and scanning electron microscopy (SEM).

All the diamond film samples studied were polycrystalline. The front surface was faceted whereas the back surface (etched back) was smoother than the front. The Raman spectrum of a sample is shown in Fig. 2; the spectra from the front and back surfaces of the film were identical. All the diamond films showed the characteristic first-order Raman spectral line around 1332 cm^{-1}. In addition, a broad fluorescence background centered around 1550 cm^{-1} is also observed, which is an indication of the presence of small amounts of sp^2 bonded carbon in the diamond film. The absorption coefficients of these diamond film windows at 532 and 1064 nm measured using a Perkin–Elmer spectrophotometer were 3.93×10^3 and 1.20×10^3 cm^{-1}, respectively. These high values again indicate the presence of highly absorbing sp^2 bonded carbon.

In Fig. 3 we show the results of laser damage on diamond film windows for 532 and 1064 nm laser radiation with a spot size of 320 μm in diameter. The output signal from the lock-in amplifier is plotted against the laser energy density. The film thickness was 1.87 μm. It can be seen that the laser

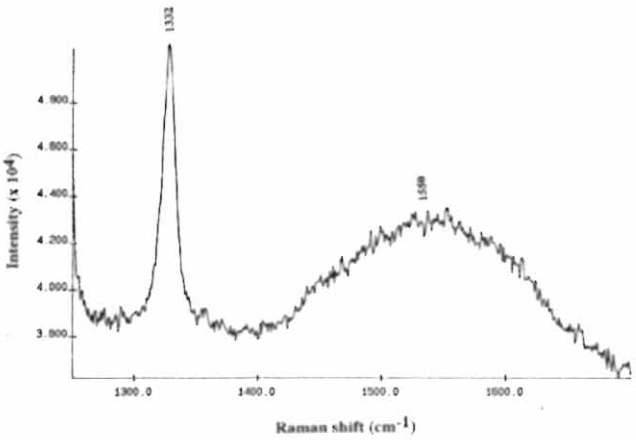

FIG. 2. Raman spectrum of a diamond film.

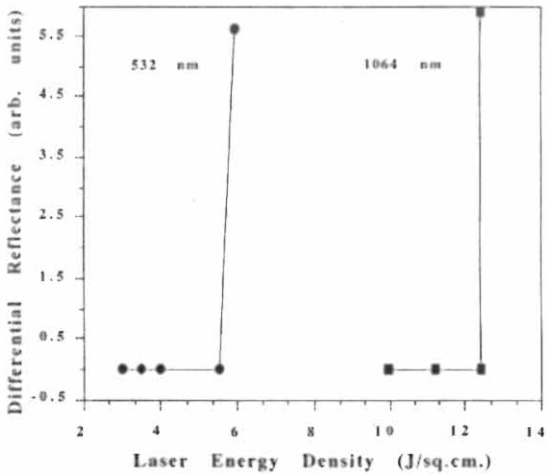

FIG. 3. Differential reflectance vs laser damage energy density for diamond film windows for 532 and 1064 nm laser radiation.

damage thresholds at 532 and 1064 nm are 6.0 J/cm^2 (300 MW/cm^2)and 12.4 J/cm^2 (620 MW/cm^2), respectively. The irradiated spots were examined using a low-power optical microscope for laser-induced damage, and the threshold energy agreed with that determined by the reflectance technique. At and above the threshold energy, laser irradiation produced holes in the diamond film windows where the film had ablated. SEM examination showed no signs of melting at the edges of the holes. In general, laser damage on thin films is due to either dielectric breakdown induced by the electric field of laser radiation or melting induced by the absorption of laser energy by impurities in the film. For the former, the laser power density P is related to the dielectric breakdown field E by the equation,

$$P = E^2 n / Z_0,$$

where n is the refractive index and Z_0 is the impedance of free space. For bulk diamond, the above equation gives a threshold of 600 GW/cm^2. For 10.6 μm laser radiation a threshold of 4 GW/cm^2 has been measured for bulk diamond.[13] Based on the self-focusing effect, the damage threshold at 1.06 μm has been estimated to be 2.97×10^{12} W/cm^2 for bulk diamond.[14] The damage thresholds measured for the diamond film windows were lower than the estimated values given above. We believe that the diamond film windows were damaged by ablation of the diamond films caused by high absorption due to sp^2 bonded carbon. The grain boundaries and defects in the film may enhance the absorption leading to low damage threshold.

Similarly, the laser damage experiments were performed on uncoated and diamond coated Si substrates. The measured damage thresholds of silicon substrates were 2.1 J/cm^2 (105 MW/cm^2) and 5.3 J/cm^2 (265 MW/cm^2) for 532 and 1064 nm laser pulses. These are within the range of values reported for silicon.[15] The absorption coefficients of silicon at these wavelengths are high, and energy transfer by resonant surface plasmons has been considered as a damage mechanism.[16] The measured damage thresholds for a silicon substrate coated with a 1.87 μm diamond film were 3.65 J/cm^2 (182 MW/cm^2) at 532 nm and 14.4 J/cm^2 (720

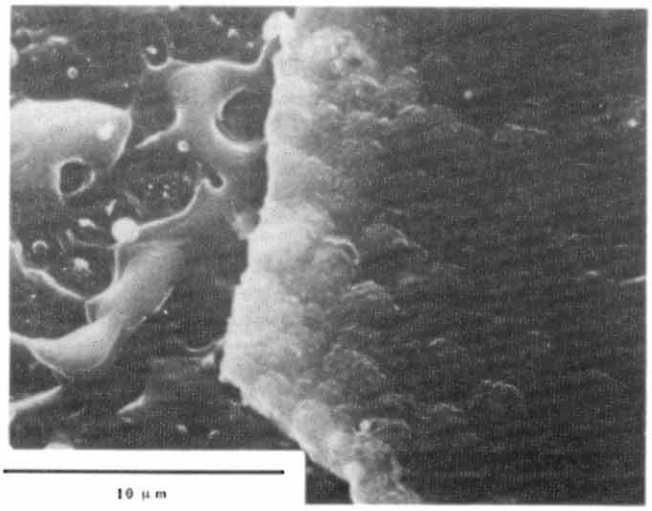

FIG. 4. SEM of a damage spot on diamond coated Si illustrating melting of Si and ablation of diamond film.

MW/cm^2) at 1064 nm. The substrate-film combination was not optimized for reflectance or transmittance. An improvement of nearly threefold in damage threshold at 1064 nm was obtained for this sample compared to the uncoated Si substrate. Thin films of oxides and fluorides having high damage threshold often used in optical coating have at least three orders of magnitude lower absorption coefficient than those measured for our films; yet the diamond films have damage threshold comparable to the values of these films. We believe this is due to the high thermal conductivity of the diamond films. A high value of thermal conductivity has been shown to be beneficial in achieving a high laser damage threshold.[17] The SEM examination of the damaged regions on the diamond coated silicon samples showed signs of melting of the substrates whereas no sign of melting was visible on the diamond film. This is clearly illustrated by the SEM photograph in Fig. 4. Experiments are under way to reduce sp^2 bonded carbon content of diamond films in order to achieve higher damage thresholds.

In 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 as an undercoat for antireflectors.[18] However, the experimentally measured damage threshold was found to be lower than the calculated values. The diamond films were ablated by the laser irradiation. The damage threshold of silicon substrate has been enhanced by diamond film coating. Better quality diamond films will be most useful for laser hardening applications.

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[1]M. W. Geis, D. D. Rathman, D. J. Ehrlich, R. A. Murphy, and W. T. Lindley, IEEE Electron Device Lett. **EDL-8**, 341 (1987).
[2]J. F Prins, Appl. Phys. Lett. **41**, 950 (1982).
[3]P S. Panchhi and H. M. Van Driel, IEEE J. Quantum Electron. **QE-22**, 101 (1986).
[4]S. C. Rand and L. G. DeShazer, Opt. Lett. **10**, 481 (1985).
[5]W. F.Krupke, M. D. Shinn, J. E. Marion, J. A. Caird, and S. E. Stokowski, J. Opt. Soc. Am. B **3**, 102 (1986).
[6]M. Sokolowski, A. Sokolowska, B. Gokieli, A. Michalski, A. Rusek, and Z. Romanowski, J. Cryst. Growth **47**, 421 (1979).
[7]B. V.Spitsyn, L. L. Bouilov, and B. V. Derjaguin, J. Cryst. Growth **52**, 219 (1981).
[8]S. Matsumoto, Y. Sato, M. Tsutsumi, and N. Setaka, J. Mater. Sci. **17**, 3106 (1982).
[9]A. Sawabe and T.Inuzuka, Thin Solid Films **137**, 89 (1986).
[10]D. V.Fedoseev, V. P. Varnin, and B. V. Deryagin, Russ. Chem. Rev. **53**, 435 (1984).
[11]Y. Hirose and Y. Terasawa, Jpn. J. Appl. Phys. **25**, L519 (1986).
[12]K. Suzuki, A. Sawabe, H. Yasuda, and T. Inuzuka, Appl. Phys. Lett. **50**, 728 (1987).
[13]R. M. Wood, *Laser Damage in Optical Materials* (Adam Hilger, Bristol, 1986), p. 114.
[14]P. Liu, R. Yen, and N. Bloembergen, IEEE J. Quantum Electron. **QE-14**, 574 (1978).
[15]R. M. Wood, *Laser Damage in Optical Materials*, (Adam Hilger, Bristol, 1986), p. 3.
[16]R. M. Walser, M. F. Becker, and D. Y. Sheng, in *Laser Induced Damage in Optical Materials:1981*, edited by H. E. Bennet, A. H. Guenther, D. Milam, and B. E. Newman, Nat. Bur. Stand. (U.S.) Spec. Pub. **638**, 103 (1983).
[17]M. R. Lange, J. K. McIver, A. H. Guenther, and T. W. Walker, in *Laser Induced Damage in Optical Materials:1982*, edited by H. E. Bennet, A. H. Guenther, D. Milam, and B. E. Newman, Nat. Bur. Stand. Spec. Pub. **669**, 380 (1984).
[18]D. H. Gill, B. E. Newman, and J. McLeod, in *Proceedings of the 9th Annual Symposium on Optical Materials for High Power Lasers: 1977*, edited by A. J. Glass and A. H. Guenther, Nat. Bur. Stand. (U.S.) Spec. Publ. **509**, 248 (1977).