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Observation of liquid carbon on diamond films under pulsed IR and UV laser irradiation

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In pulsed laser processing of synthetic diamond films it is an open question whether there exists temporarily a liquid phase of carbon under the influence of high temperature and pressure or not. Such a liquid phase would show an enhanced mobility of electrons and therefore a metal-like behavior. This would result in an increased reflectivity. We measured the time-resolved reflectivity of diamond films during pulsed laser irradiation at 193 nm and 1064 nm. At 193 nm significantly increased values for a period of typically 200 ns were found in the fluence range 15–60 J/cm^2. With irradiation at 1064 nm an evident increase was observed only in the fluence range of 23 J/cm^2. The same experiments were performed with silicon. In this case the melting under pulsed laser irradiation is well established. Silicon showed at both wavelengths a rise in reflectivity. By comparison, the existence of a thin metallic, liquid-carbon layer is deduced for irradiation of diamond films at 193 nm and, within a narrow fluence regime, also at 1064 nm.

I. INTRODUCTION

In the study of the basic processes taking place during laser modification of diamond films it is an interesting question whether carbon melts or not. The modifications of elemental carbon form bonds with high energies. Therefore the melting temperature is very high as indicated in the phase diagram.[1,2] Attempts have been made to calculate the properties of liquid carbon as well as the boundary of the region of its existence in the phase diagram.[2,3] Experiments on the investigation of the liquid phase of carbon have been conducted with graphite as starting material.[3–6] Picosecond reflectivity measurements suggest a semi-insulating phase,[5] but more recent studies promote the conclusion that liquid carbon is metallic with a high electrical conductivity.[6]

These experiments have been carried out using graphite which exhibits a very low thermal conductivity along its *c* axis compared to its in-plane value. When the sample is heated by pulsed laser radiation incident parallel to the *c* axis, this leads to relatively low threshold fluences for melting (less than 1 J/cm^2). Results have been obtained recently showing that melting is also possible when a diamond sample with its high, isotropic thermal conductivity is used.[7] Here we report in detail on the time-resolved reflection of a continuous wave (cw) Ar-ion probe laser beam at the surface of a synthetic diamond film which was irradiated by pulses from either an ArF or a Nd:YAG laser.

II. EXPERIMENTAL PROCEDURES

The schematic setup for time-resolved reflectivity measurements during pulsed laser ablation is presented in Fig. 1. Either an ArF ($\lambda=193$ nm) or a Nd:YAG ($\lambda=1064$ nm) laser was used as material-processing radiation source. The pulse duration was approximately 20 ns in both cases. The fluence on the sample was in the range 13–63 J/cm^2, the angle of incidence was constantly 80°. This is the optimum angle for laser polishing of diamond films.[8] The sample was a 20 μm thick chemical-vapor-deposited diamond film on a tungsten substrate. For comparison a silicon (100) wafer was also irradiated. The cw probe beam, supplied by an Ar-ion laser ($\lambda=514.5$ nm), was focused on the same spot on the sample as the processing beam, however at almost normal incidence. The specularly reflected part of the probe beam was analyzed in a monochromator with 0.05 nm full width at half maximum resolution and finally detected using an avalanche photodiode receiver with a frequency response from dc to 100 MHz.

The experimental difficulty is the plasma luminescence which is very strong in the fluence regime used in this investigation. Its spectrum consists of a continuum with superimposed line spectra from the involved elements. For a usable signal-to-noise ratio a combination of serious restriction on the detector passband ($\Delta\lambda=0.05$ nm), a high probe laser beam irradiance (200 W/cm^2 in the focus), and limitation to the specularly reflected part of the probe beam proved to be essential.

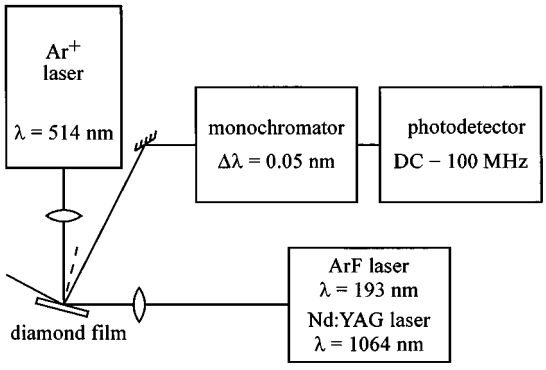

FIG. 1. Setup for time-resolved reflectivity measurements of diamond during pulsed laser ablation.

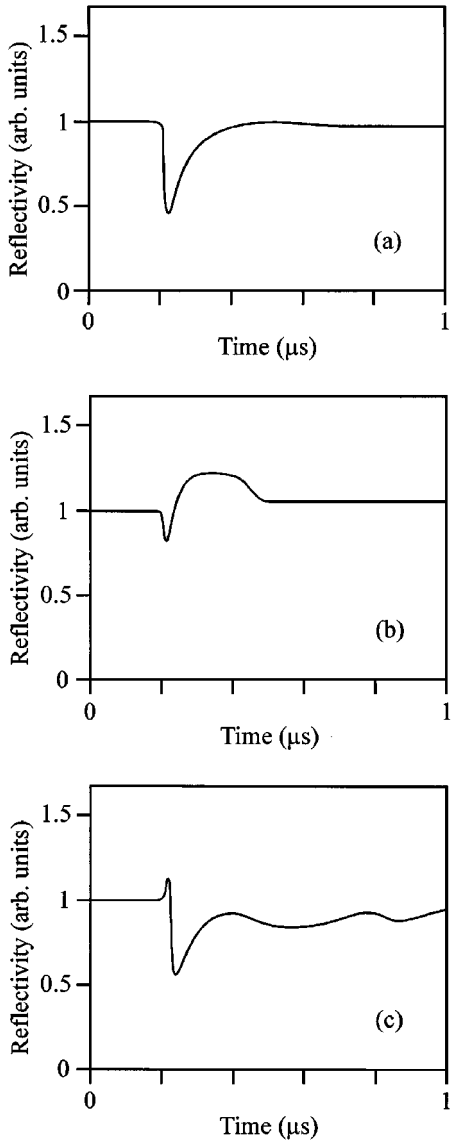

FIG. 2. Reflectivity versus time of a diamond film irradiated with the Nd:YAG laser at a fluence of (a) 13, (b) 23, and (c) 63 J/cm^2.

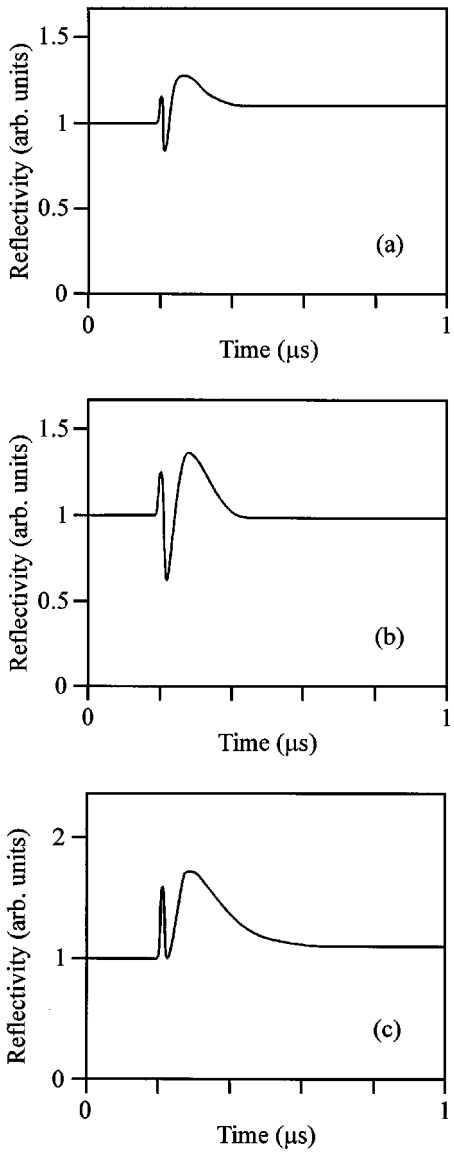

FIG. 3. Reflectivity versus time of a diamond film irradiated with the ArF laser at a fluence of (a) 15, (b) 30, and (c) 60 J/cm^2.

III. RESULTS AND DISCUSSION

Figure 2 shows the specular reflectivity of a diamond film during pulses of different fluences from the Nd:YAG laser. The steady-state reflectivity before the laser pulse is normalized to 1. The final reflectivity can be different from its previous value, 1, for the laser pulse may change the surface properties. For this reason the term reflectivity instead of reflectance is used. The laser pulse starts at time $t=0.2$ μs in the graphs. This also applies to Fig. 3 which depicts the specular reflectivity of a diamond film irradiated with the ArF laser at various fluences. For comparison the reflectivity of a silicon wafer irradiated with the ArF laser is presented in Fig. 4 (note the altered time scale).

First consider the measurements with the Nd:YAG laser. Typical representants for fluences of 13, 23, and 63 J/cm^2 are shown in Figs. 2(a), (b), and (c), respectively. At 13 J/cm^2 essentially a transient drop of reflectivity can be seen upon a laser pulse. At 23 J/cm^2 a short-lived drop of the reflectivity is visible, followed by an increase lasting approximately 200 ns with its maximum at 1.2 times its steady-state value. At a fluence of 63 J/cm^2 a very different signal is obtained. After an initial drop a long-lasting irregular signal is found.

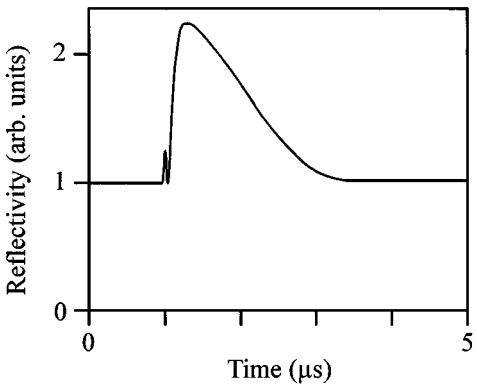

FIG. 4. Reflectivity of a Si wafer during ArF irradiation at a fluence of 16 J/cm^2.

The reflectivity drop at the beginning is assumed to be mainly caused by partial absorption and reflection of the probe laser beam at the plasma. In the case of Fig. 2(a) we also expect a contribution from graphitized diamond which evaporates due to the high temperature. The reflectivity peak of Fig. 2(b) is assigned to a transient layer of liquid carbon. This will be discussed in conjunction with the measurements with the ArF laser. The irregular signal in Fig. 2(c) is probably due to diamond particles popping off the laser focal spot since damage to the diamond film easily occurs at such a high fluence at 1064 nm. The reason for this is the radiation absorption length α^{-1}, which is of the order of the film thickness. Thus, a considerable part of the laser fluence reaches the diamond-substrate interface and may lead to delamination of the diamond film due to a mismatch of the thermal-expansion coefficients.

Figure 3 shows the reflectivity as a function of time of a diamond film irradiated with the ArF laser at fluences of (a) 15, (b) 30, and (c) 60 J/cm^2. The sharp positive spike in each graph indicates the location of the laser pulse. After that, at 15 J/cm^2, the reflectivity drops below 1, but increases within typically 40 ns to its maximum value of 1.3 and then approaches the steady-state reflectivity during the next 200 ns. At 30 J/cm^2, after a pronounced drop below 1, the reflectivity reaches a maximum of 1.4 before it returns to 1. The high-fluence shot (60 J/cm^2) does not exhibit a drop below 1, but reaches a maximum of 1.7. The following decay time appears to be slightly longer.

As with the Nd:YAG measurements the reflectivity changes are hidden by the plasma during $\sim$50 ns. However, the plasma induced by the ArF laser shows a very bright luminescence which contributes to the narrow positive spikes. Moreover, the plasma is denser than with the Nd:YAG laser and is capable of reflecting the probe beam at 514 nm. The density of a plasma increases with the frequency of the laser which generates the plasma. As soon as the plasma density surpasses the critical density corresponding to the frequency of the probe beam, the latter is reflected and absorbed by the plasma. The surface of the critical density for the probe beam can be curved and move away from the diamond film because of the plasma expansion, which temporarily leads to a geometrical misalignment with a corresponding detector signal loss.

When the plasma becomes transparent to the probe beam a reflectivity peak lasting approximately 200 ns is detected in Fig. 2(b) and Fig. 3. It is attributed to the liquid state of carbon which is metallic.[6] This can be made plausible in several ways:

(1) With the ArF laser the reflectivity peak grows continuously with fluence. We did not observe this dependence with the Nd:YAG laser because of the narrow fluence range for the possible generation of liquid carbon. On the one hand, the high absorption length of diamond at 1064 nm requires a high fluence in order to achieve the temperature of the graphite-liquid-gas triple point. On the other hand, a high fluence produces a dense plasma which is opaque to its generating radiation; the diamond film is shielded from the laser pulse. In the case of irradiation with the ArF laser this fluence range is much wider because of the small absorption length (a low fluence is sufficient for reaching the melting conditions) and the high critical density of the plasma (a high fluence is required for shielding). It is difficult to estimate the thickness of the liquid layer from the available reflectivity data because the course of the reflectivity at the beginning, where we expect the maximum, is hidden and cannot be extrapolated. However, in the case of the ArF measurements, a strong increase of reflectivity with fluence and the supposed metallic character of liquid carbon indicate that the thickness is not more than a small multiple of the absorption length α^{-1}. The value of α^{-1} is likely in the same range as of a real metal, e.g., 20 nm for gold as can be calculated from the complex index of refraction. Another approach considers the ablation depth per laser pulse. The liquid layer must either evaporate or resolidify in a nondiamond form of carbon. During the cool-down diamond still converts to graphite when the temperature is above $\sim$1200 K. Since there is no indication that graphite piles up even after thousands of laser pulses we deduce that it must have been etched except for a thin remaining layer. Therefore, assuming equal densities of liquid carbon and diamond at room temperature, the liquid layer cannot be thicker than the ablation depth per laser pulse. For ArF irradiation incident under an angle of 80° we measured an ablation depth of 30 nm per pulse at 20 J/cm^2 and extrapolate a value of 90 nm at 60 J/cm^2. We consider these values as upper limits for the depth of the liquid. They correspond quite well with calculations of Ref. 3 (with graphite as starting material) which yield up to several 100 nm.

(2) A coarse estimation of the temperature at the diamond film surface can easily be obtained. We assume a layer of thickness d being heated up homogeneously during a laser pulse of duration τ. The thickness d is determined by the absorption length α^{-1} and the heat diffusion length l. For simplicity the larger of these values is taken for d. Neglecting the energy transfer from the plasma, the blackbody radiation and the latent heat of the phase transition, the temperature increase ΔT caused by the fluence F and the absorptance A immediately upon termination of the laser pulse is

$$\Delta T = \frac{AF}{c_p \rho d}, \tag{1}$$

assuming all values to be independent from temperature. The heat capacity c_p is 0.52 J/g K and the density ρ equals 3.5 g/cm^3. The absorptance A takes a value of 0.57 for an angle of incidence of 80° for both wavelengths, since the dependence from the refractive index is negligible at such high angles. The heat diffusion length $l = 2\sqrt{\chi \tau}$ can be computed from the heat diffusion constant $\chi = 2.3$ cm^2/s,[9] and the pulse duration $\tau = 20$ ns, which yields $l = 4.3$ μm. In the case of ArF radiation, l is clearly larger than the absorption length $\alpha^{-1} = 1.6$ μm for type-IIa diamond, thus $d = l$. For Nd:YAG irradiation, α^{-1} is of the order of 20 μm (depending on the film quality), therefore $d = \alpha^{-1}$.

The graphite-liquid-gas triple point lies at about $T = 4400$ K, $p = 10$ MPa.[6,1] Assuming $\Delta T = 4400$ K a threshold fluence $F_{\text{th}} \approx 6$ J/cm^2 can be calculated from Eq. (1) for the ArF laser and $F_{\text{th}} \approx 28$ J/cm^2 for the Nd:YAG laser. These values are compatible with the increase of the reflectivity observed at 15 and 23 J/cm^2, respectively. The condition on the pressure

is fulfilled since a plasma is generated at this fluence, and a thin layer of liquid carbon should be produced.

(3) For comparison a silicon sample was exposed to ArF laser radiation. The result shown in Fig. 4 is similar to that of diamond depicted in Fig. 3 except for the longer decay time of the peak. This can be explained by a higher heat capacity and a lower thermal conductivity of silicon. Since silicon is known to melt when irradiated with intense laser pulses,[10] the same is assumed for diamond.

For these reasons we deduce the observation of metallic liquid carbon in the vicinity of the graphite-liquid-gas triple point.

IV. CONCLUSIONS

We have measured the time-resolved reflectivity of a chemical-vapor-deposited diamond film during laser ablation with either ArF or Nd:YAG laser pulses. In the case of the ArF laser, a strong increase of the reflectivity up to 1.7 times its regular value during 200 ns is attributed to a liquid, metallic carbon phase. This is inferred from a monotonic dependence of the maximum reflectivity from the applied fluence, from the duration of enhanced reflectivity which is much longer than the laser pulse and the plasma luminescence, from an estimation of the diamond surface temperature, and from a comparison with silicon which shows a similar reflectivity behavior and of which the melting is well established. The thickness of the liquid-carbon layer is estimated to range from 30 to 90 nm. A threshold fluence of 6 J/cm^2 has been estimated for the melting of diamond films. With Nd:YAG irradiation melting signatures have been found only at a fluence of 23 J/cm^2. Higher fluences lead to plasma shielding, and lower values do not sufficiently heat the diamond film.

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