Laser induced breakdown spectroscopy (LIBS) is a powerful analytical tool that provides standoff elemental analysis of a wide variety of materials in solid, liquid, and gaseous states without any sample preparation [1,2]. A typical LIBS spectrum consists of a set of discrete atomic and ionic lines superimposed on a broad continuum [3,4]. Much of the research on LIBS is directed toward understanding the origin of the continuum and finding means of suppressing it in order to increase the signal/background (S/B) ratio. It is generally found that the continuum is much shorter lived than the discrete spectrum. This property allows the background to be suppressed by gating the detector [5,6]. The optimal start and stop times of the detection window are sensitive to the choice of target material [6,7] (which is not necessarily known in advance), the laser properties (wavelength, pulse duration, and focal point), and the specific elements to be detected. A better strategy might be to find a means of filtering out the continuum while minimally affecting the discrete spectrum.

Recently we reported that the continuum produced by the ablation of solid targets in air with a femtosecond laser pulse is strongly polarized, with the magnitude of the polarization reaching values in excess of 95% for wavelengths <350 nm, while the lines have little or no polarization [8]. This property was observed for various metals [9,10], semiconductors [8], and dielectrics [10], including crystalline and amorphous materials, and appears to be a general property of solid matter. By placing a polarizer before the detector, it is possible to greatly attenuate the continuum while having little effect on the discrete lines. We refer to this technique as polarization-resolved LIBS, or PRLIBS. Apart from its practical utility, polarization of the plasma continuum is of fundamental interest as a hitherto unexplored property of laser-matter interactions.

Extension of the PRLIBS technique to the femtosecond regime could be of great utility, since LIBS measurements are most commonly performed on this time scale. The emission of polarized light implies that the electrons generating the light must be oscillating in some preferred direction. Such directional-
It is interesting to compare these results with our earlier findings for femtosecond excitation. As shown in Fig. 2, the discrete lines again appear as minima in the polarization spectrum, but in this case the continuum polarization reaches a maximum value close to 100% and falls off at long wavelengths.

Figure 3 shows the dependence of the polarization and PRLIBS spectra on laser fluence. We find that while $P$ decreases with fluence, the S/B ratios for different peaks remain fairly constant, having values $\sim 1–2$ without the polarizer and $\sim 5–7$ with the polarizer. Similar behavior was found in the femtosecond-PRLIBS spectra of Si [8] and Al [9]. Figure 4 shows the effect of the focal point on the PRLIBS spectrum. The upper panel shows the unfiltered spectrum taken with the laser focused above the surface ($z = -0.5$ and $-0.25$ mm), on the surface ($z = 0$), and beneath the surface ($z = 0.25$ and 0.5 mm). For $z \leq 0$ the continuum completely obscures the discrete spectrum and saturates the detector. Previous nanosecond-LIBS studies [11,12], as well as our earlier femtosecond-LIBS study [9], also obtained the best S/B for focusing beneath the surface. With the polarizer in place (middle panel), the line spectrum is well resolved, with the largest S/B occurring for $z = 0.25–0.5$ mm. As found previously for femtosecond-PRLIBS, the effect of the polarizer is to make the spectrum much less sensitive to focal position, a property that could be useful for standoff detection.

From the polarization spectra it is obvious that the discrete and continuum emissions are generated by very different processes. The line spectrum is very likely produced by discrete electronic transitions of atoms and ions in the ablation plume. Polarized emission caused by nonstatistical distributions of magnetic sublevels is readily suppressed by randomizing collisions. The continuum emission, on the other hand, is generally attributed to free–free Bremsstrahlung collisions and bound–free electron recombination reactions [4]. Anisotropy in the velocity distribution of the electrons is transformed into
polarization of the emitted photons [13]. Such processes are much faster than the radiative and collisional decay of electronically excited atoms and ions, and, indeed, the decay time of the continuum emission is found to be much shorter than that of the discrete spectrum in both the nanosecond [14] and femtosecond [14,15] regimes. This property is illustrated dramatically in Fig. 5, where the decay time is plotted in 1 nm intervals. These data were obtained from exponential fits to the time-resolved fluorescence measured with a photomultiplier tube (R212, Hamamatsu Photonics, 50Ω load) attached to the output of the spectrograph. A plot of the decay time versus wavelength strongly resembles the PRLIBS spectrum, and at some wavelengths it displays even greater spectral resolution. Although it takes 2 orders of magnitude more time to acquire, the decay time spectrum is potentially a useful new spectroscopic tool. The shortest measured decay time of the continuum is 10 ns, which exceeds the pulse width of the laser. This result is surprising in that it suggests that the anisotropy of the electron velocity distribution survives multiple atmospheric collisions. A possible explanation is that the recombination reaction is the rate-limiting step, and randomizing collisions rapidly quench the emission, so that any emitted photons are detected before the anisotropy is lost.

The decline of $P$ with fluence indicates that the electronic anisotropy is diminished at higher plasma temperature. For the discrete emission, the electronically excited species survive multiple collisions before emitting a photon, and any initial polarization is substantially reduced.

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References