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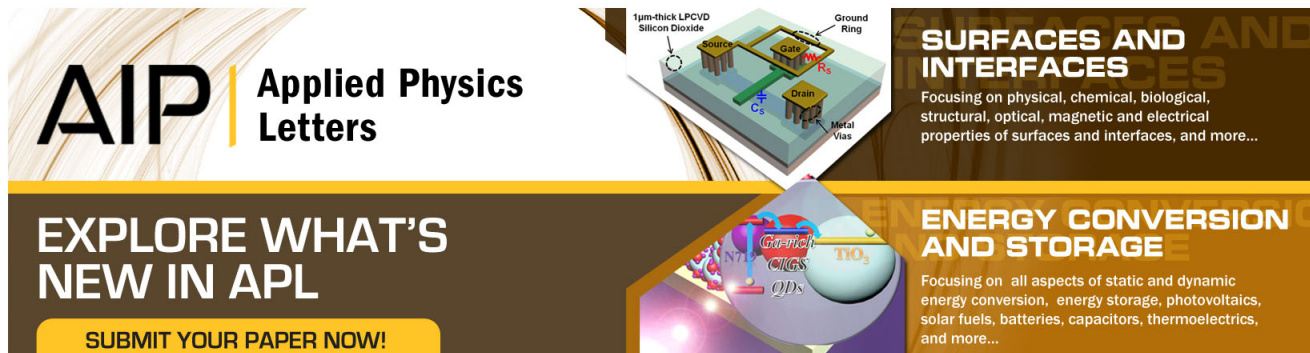Journal Homepage: http://apl.aip.org/

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Hole burning spectroscopy of R' aggregate color centers in polycrystalline LiF thin films using a GaAlAs diode laser

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The first spectroscopic measurements of R' aggregate color centers contained in polycrystalline LiF hosts are reported. The inhomogeneous and homogeneous widths of the 830-nm zero phonon line are measured by conventional grating spectroscopy and by photochemical hole burning spectroscopy using a current tuned GaAlAs diode laser with 3-mW output power. An extensive photochemical hole burning comparison between single and polycrystalline samples is presented.

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The cryogenic phenomenon of photochemical hole burning makes it possible to perform solid state spectroscopy at resolutions far beyond the limits set by inhomogeneous broadening. Narrow persistent spectral holes are produced in inhomogeneously broadened absorption bands of photoactive molecules upon exposure to a narrowband laser.[1]

By tuning the laser to a selected frequency within the inhomogeneous line, only a subset of active species will have their homogeneous absorption line resonant with the defined laser wavelength. This selective laser excitation will deplete the population of the subset, producing a persistent hole or dip in the absorption band. This phenomenon can be successfully applied to store bits of information in frequency domain optical memories.[2] These memories allow the optical frequency to be utilized as an additional dimension for the organization of optical memories.

One of the most promising storage materials for frequency domain optical memories are the aggregate color centers in alkali halide hosts. At low temperatures the absorption spectra of these centers present sharp and strong inhomogeneously broadened zero phonon lines (ZPL). In single crystals it has been shown that it should be possible to burn 10^3 holes in the inhomogeneous line and thus to store 10^3 bits of information at each spatial storage location.[3]

Polycrystalline thin-film samples present two advantages for such storage applications. The thin-film geometry is consistent with the depth of focus of laser beams defined by the diffraction limited optics. Also, the inhomogeneous linewidth is directly related to the local environment in the host material and it can be increased by appropriate thin-film preparation conditions.[4]

GaAlAs diode lasers also have many advantages for this type of optical storage application.[5] They are compact, reliable, have modest power requirements, operate in a single longitudinal and transverse mode with no external cavity, and can be rapidly tuned by varying the injection current.

In this letter we report the first photochemical hole burning in thin-film polycrystalline samples using GaAlAs diode lasers. The material used was LiF containing R' aggregate color centers which exhibit an inhomogeneous broadened zero phonon line centered at a vacuum wavelength of 830 nm. The R' center is a negatively charged intrinsic aggregate color center consisting of three trigonally arranged anion vacancies surrounded by four trapped electrons. (In more modern notation, the R' center is known as the F_3^- center.) Photochemical hole burning in this line for single crystal samples has previously been demonstrated using both IR dye lasers[6] and GaAlAs diode lasers.[7] A comparative study of the spectral characteristics of polycrystalline and bulk single crystal is presented.

The polycrystalline samples were vacuum evaporated from LiF powder (Balzers) onto Corning glass substrates of 5 mm diameter. The LiF powder contained impurities like Fe (< 100 ppm) and Pb (< 50 ppm). The grain sizes of the films were analyzed by scanning electron microscopy and had an average value of 1 μm. The film thickness was 20 μm. The single crystal sample was a $6 \times 5 \times 3$ mm thick crystal of LiF doped with 0.05 mole % MgF_2. (The Mg^{++} divalent impurities resulting from the doping served to stabilize the aggregate color centers.[8]) The R' centers in both types of samples were produced by x-ray irradiation at room temperature.

The zero phonon line corresponding to the R' color center has a Gaussian line shape due to inhomogeneous broadening. The inhomogeneous line shape was measured by conventional emission and absorption grating spectroscopy for both the single and polycrystalline samples. The full width of half-maximum of the inhomogeneous line was found to vary from 0.5 nm in the single crystal to 3.0 nm in the polycrystalline sample. This additional broadening can be attributed to energy level shifts caused by the extra strain due to the many grain boundaries in the polycrystalline sample. Absorption spectra showed that the 3-mm-thick crystal sample had a 30% deep ZPL whereas the 20-μm-thick polycrystalline sample had a 3% deep ZPL.

The relative concentrations of the color centers in the two types of samples can be estimated using Smakula's formula[9] to relate the number of centers/cm^3 to the half-width of the zero phonon line, the absorption coefficient, and the oscillator strength. If the oscillator strength is assumed to be the same, the density of R' centers in the polycrystalline sample is found to be 90 times higher than in the single crystal
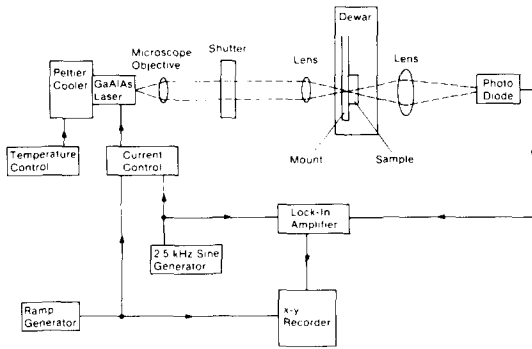
FIG. 1. Experimental setup to study photochemical hole burning using GaAlAs diode lasers.

samples. This result is reasonable, since the surface and grain boundaries are well established vacancy sinks.

Figure 1 shows the experimental setup used for photochemical hole burning in single and polycrystalline samples with a GaAlAs diode laser. The beam of a Mitsubishi 3001 TJS GaAlAs diode laser was collimated by a 0.5-N.A. microscope objective and focused onto the samples which had been immersed in a He dewar at 2 K. The comparison study was done by sliding the sample holder inside the dewar without changing the optical path of the laser beam. The transmitted beam was focused onto a fast *pin* photodiode (Motorola MRD 510). The optical intensity for burning and detecting the holes was adjusted by attenuators. The exposure time was controlled by a mechanical shutter. The burning was accomplished by tuning the laser to fixed wavelength within the zero phonon line and exposing the samples to 2 - mW laser power. The detection of the holes was accomplished by slowly tuning the laser through the hole location in frequency space while dithering the laser sinusoidally at 2.5 kHz. A lock-in amplifier detected this Fourier component of the signal from the photodiode which is proportional
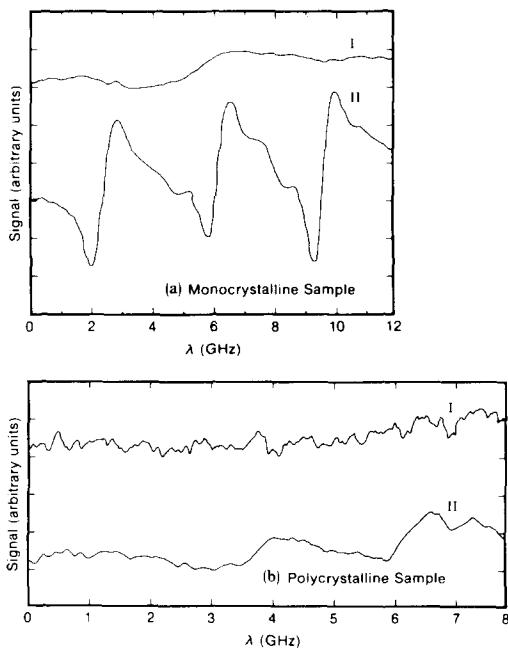
to the first derivative of the absorption feature.[7,10] In all experiments for reading, the laser power was attenuated with a 2.6 neutral density filter to about 5 μW at the sample and focused to a spot size of 1–2-mm diameter.

Figure 2 shows the detected signal for a burnt hole in both samples. Figure 2(a) presents three holes burnt for 10 s each in a single LiF:Mg^{++} crystal. Figure 2(b) shows the signals from two holes burnt for 30 s each in the polycrystalline sample.

The measured hole linewidth was a result of a convolution of the linewidth of the burning laser with the true hole width with the linewidth of the reading laser. The measured value for the width of the reading laser was 448 $\pm$ 24 MHz. This broad value is due to several factors: the natural linewidth of the laser (50 MHz), the wavelength fluctuations induced by drive current instabilities ($\sim$ 100 MHz), the resolution of the measuring etalon (150 MHz), and the modulation width ($\sim$ 400 MHz).

The experimental value of the hole linewidth was 544 $\pm$ 44 MHz for the monocrystalline LiF and 704 $\pm$ 85 MHz for the polycrystalline one. This difference is significant, however, there were insufficient data to perform a deconvolution to calculate the true hole widths.

Although the exposure time was three or more times less for the monocrystalline sample the signals from photochemical holes were about an order of magnitude stronger than in the polycrystalline sample. The hole depth in the monocrystalline sample was equivalent to about 1–3% in absorption change, thus the hole depth in the polycrystalline film is equivalent to an absorption change of about 0.2%.

This difference might be due to the higher number of active species in the monocrystalline sample with a thickness of 3 mm compared to 20 μm of the polycrystalline sample. Totally different required exposure times were observed: for

FIG. 2. Signals from photochemical holes before (I) and after (II) hole burning: (a) monocrystalline sample and (b) polycrystalline sample.
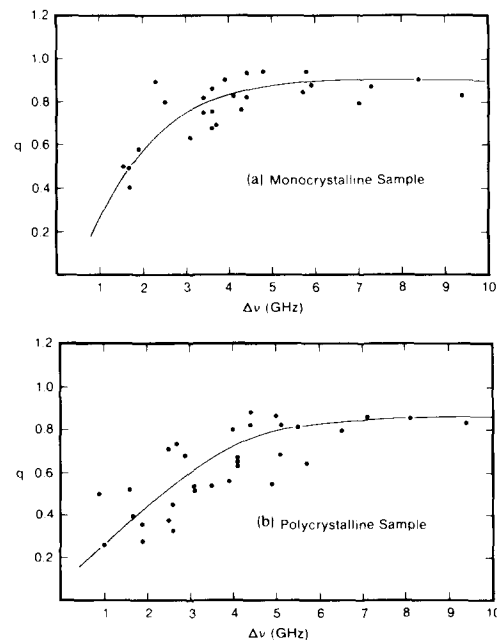

FIG. 3. Fractional remainder q of a signal from one hole after burning a second hole next to it vs the frequency offset between the two holes: (a) monocrystalline sample and (b) polycrystalline sample.
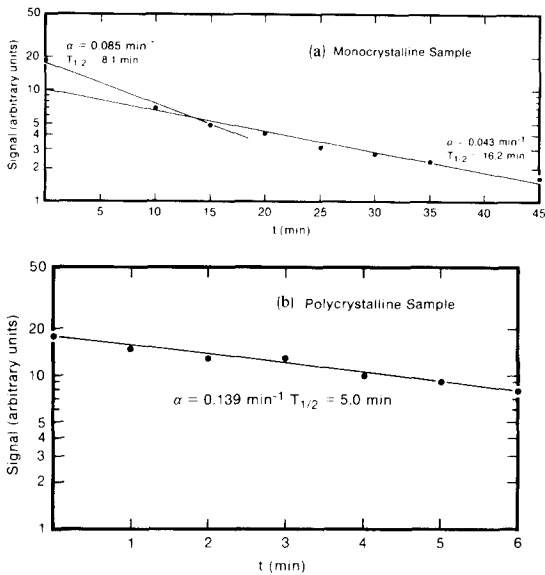
FIG. 4. Signal decrease from holes while UV erasing: (a) monocrystalline sample and (b) polycrystalline sample.

obtaining a hole in the polycrystalline film which gives a signal to noise ratio of 1 the exposure time is 1 s; however, in the single crystal with the same setup the signal to noise ratio was still about 40 even at the shortest possible exposure time of 10 ms.

Another series of experiments was conducted to study the interaction between an initially isolated hole and a second hole burnt in the same spatial location at a nearby optical frequency. The effect of this interaction was always to reduce the amplitude of the previous burnt hole to a fraction q of its former value. Figure 3 shows q versus the frequency difference between the holes for both the single crystal and the polycrystalline samples. The hole interaction decreases significantly with bigger wavelength offset between the holes. Above an offset of 5 GHz q saturates at a value of around 0.85 independent of the structure of the sample. The single crystal seems to have a slightly shorter hole interaction distance which presumably is related to the narrower hole width.

Finally, a series of experiments was conducted to compare the UV induced hole erasing behavior of the samples. The UV beam was from a mercury lamp filtered by Corning 7-60 and 0-52 filters and had maximum intensity at 364 nm. The UV radiation and the hole detecting GaAlAs laser beam were simultaneously incident on the sample so that the erasing could be monitored in real time. Figure 4 shows the logarithmic decay of the hole depth versus the UV exposure time. Figure 4(a) presents the results of the monocrystalline sample. It shows that the erasing process has two components. The time $T_{1/2}$ for the signal intensity to be reduced to half its value varies between 8.1 and 8.5 min for the fast decay in the beginning of the erasing and between 11.3 and 16.2 min for the slower decay after about 10 min. Figure 4(b) shows the erasing effect in a polycrystalline sample. It has a pure exponential behavior and is much faster than in the single crystal. It varies between 3.5 and 6.5 min.

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