Nonlinear Processes II

Optical Hole Burning and Coherent Transient *rf* Double Resonance Spectroscopy of Rare Earth Ions in Solids

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At low temperatures and concentrations hyperfine interactions provide the dominant contribution to optical homogeneous linewidths of rare earth ions in crystals. The resolution necessary to study these interactions has been obtained using optical coherent transients (e.g. photon echo), optical hole burning, and optical-*rf* double resonance. Hole burning and photon echoes allow the effects of these interactions on optical spectra to be observed directly by eliminating inhomogeneous broadening due to crystal strain fields or other static local fields. These methods have yielded measurements of hyperfine interactions in both ground and excited electronic states, and have led to increased understanding of optical dephasing in these materials. In many cases the resolution of the experiment can be further increased by using hole burning or photon echoes as probes to detect the resonance of an applied *rf* field with hyperfine splittings [1, 2]. This method can have the resolution characteristic of the *rf* resonance while retaining the sensitivity of optical techniques, and often yields information not obtainable directly.

For example, Elliott [3] predicted more than twenty years ago that the nuclear magnetic moment of the trivalent europium ion in its $^7F_0$ ground state would be anomalously small (approximately 1/10 of its usual value) due to second-order hyperfine coupling with the $^7F_1$ levels at $\sim 400\ \mathrm{cm}^{-1}$. The resulting small effective moment makes conventional NMR or NQR measurements of Eu^{3+} very difficult, and no such experiments have been reported. Using optical hole burning and optically detected NQR in $YAlO_3:Eu^{3+}$ we have measured the effective nuclear moment of ^{151}Eu and ^{153}Eu in both ground $^7F_0$ and excited $^5D_0$ states, thus verifying Elliott's prediction for the first time. The measured value in $^7F_0$ is 21% of the intrinsic value, leading to a radial hyperfine parameter of $\langle r^{-3}\rangle = 49.6 \pm 1\ \mathrm{A}^{-3}$, very close to the theoretical value of $49\ \mathrm{A}^{-3}$.

This near cancellation of the ground state nuclear moment is a general phenomenon in Eu^{3+} systems. The resulting difference in ground and excited state moments implies the possibility of a significant contribution to the optical homogeneous linewidth from hyperfine interactions in systems such as $YAlO_3:Eu^{3+}$ and $Y_2O_3:Eu^{3+}$. Photon echo dephasing measurements in these materials will also be discussed.

In these Eu^{3+} systems and in Pr^{3+} systems studied previously, hole burning occurs due to optical pumping of rare earth hyperfine levels. We have recently found that in a tetragonal site of $CaF_2:Pr^{3+}$, holes are burned by optical pumping of ^{19}F superhyperfine levels. Optical-*rf* double resonance experiments based on this phenomenon have been used to obtain magnitudes and directions of the superhyperfine fields. This information led us to infer the lattice distortion resulting from the substitution of Ca^{2+} by Pr^{3+} plus an interstitial charge compensating F^-.

In contrast to the hole burning double resonance experiments discussed above, photon echo double resonance (PENDOR) can be used to detect resonances both in ground and excited electronic states. In addition, resonances with both hyperfine and superhyperfine splittings can be detected. We have developed a PENDOR technique which differs from the previously described stimulated photon echo PENDOR [2] in that it is based on modulation of the two-pulse photon echo decay by *rf* nutation of the nuclear spins. This method has been used to measure splittings in $YAlO_3:Pr^{3+}$ and $YAlO_3:Eu^{3+}$.

1. L.E.Erickson: Opt. Commun. **21**, 147 (1977)
2. P.F.Liao, P.Hu, R.Leigh, S.R.Hartmann: Phys. Rev. A **9**, 332 (1974)
   K.Chiang, E.A.Whittaker, S.R.Hartmann: Phys. Rev. B **23**, 6142 (1981)
3. R.J.Elliott: Proc. Phys. Soc. (London) B **70**, 119 (1957)

Tunneling and Relaxation Processes in Organic Glasses as Studied by Photochemical Hole Burning

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Optical high resolution experiments such as photochemical hole burning (PHB) or fluorescence line narrowing (FLN) have, in the past years, been used to shed light on the properties of amorphous solids. Some of the least understood aspects of the physics of amorphous materials are relaxation processes (T_1, T_2) and tunneling processes at low temperatures.

In the following the reversible proton-transfer photochemistry of quinizarin is used to perform PHB experiments in glasses [1]. The dye molecule quinizarin is doped into organic alcohol glasses at a concentration of about 10^{-5} mole/mole. For studying the dynamic processes, details of the "hole spectra" in the electronic zero-phonon origin of the molecule are investigated at liquid helium temperatures. Similar studies on the related phonon bands of the spectra have been reported earlier [2, 3]. They have been used to study electron-phonon coupling parameters of amorphous host materials.

Figure 1a shows a typical PHB spectrum at 5 K; the hole appears as narrow dip (width $\approx 1\ \mathrm{cm}^{-1}$) on the broad absorption background of the inhomogeneously broadened $S_1 \leftarrow S_0$ transition (width $\approx 700\ \mathrm{cm}^{-1}$). If one measures the temperature dependence of the "hole spectrum" the following observations are made:

α) The lineshape can be approximated by a Lorentzian; its width follows a quadratic law $\Gamma(T) = \Gamma_0 + cT^2$.

β) The line does not regain its original width after a thermal cycle from 5 K to 20 K (see Fig. 1).

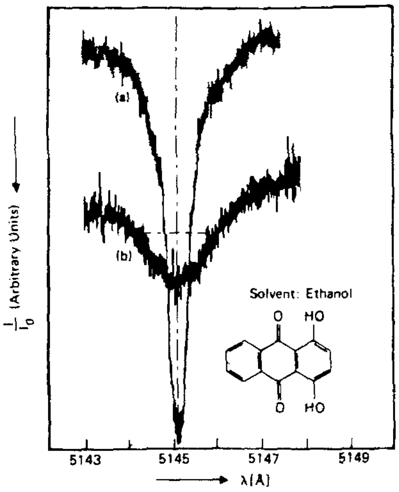

Fig. 1a and b. Photochemical hole at 5 K before (a) and after (b) thermal cycling

γ) There is a rather large residual linewidth at $T=2$ K.

In order to reconcile the first two observations, one has to invoke two contributions optical linewidth. A first contribution which is reversible and which reflects a true dephasing process (T_2). One would expect that this contribution to the linewidth could be measured in an echo-type experiment. To our knowledge, experiments of this kind have only been performed with crystalline systems [4]. The second contribution to the linewidth is an irreversible part; i.e. the linewidth does not regain its original width after a complete thermal cycle. This part will be explained in terms of a redistribution among the tunneling levels of the amorphous matrix [5, 6]. The redistribution of tunneling levels leads to a "spectral diffusion" of the states whose absorption was originally centered at the laser frequency. If one analyzes the irreversible part of the linebroadening in terms of a thermal equilibration of the two-level systems (TLS), one can obtain information about the distribution function of the TLS (5). The most revealing part of the experiment is the fact that the TLS distribution function is rather narrow (several cm^{-1}) quite in contrast to the width of the inhomogeneous site distribution ($10^3\,\mathrm{cm}^{-1}$).

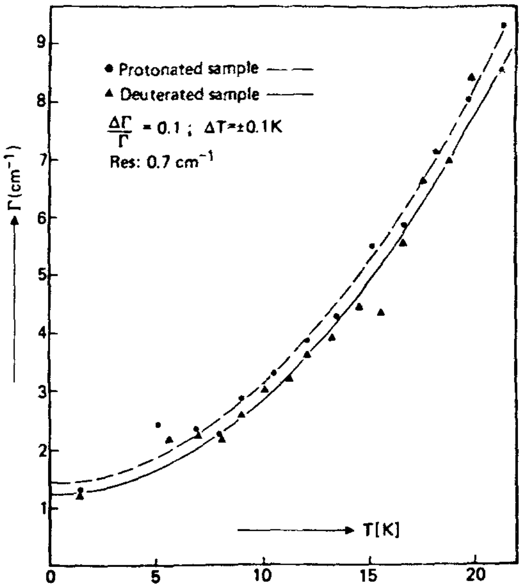

Fig. 2. Temperature dependence of the photochemical holes

The rather large residual line-width for $T\to 0$ is still a puzzle. It will be discussed under two possible hypotheses: TLS redistribution processes or picosecond dephasing processes at 2 K. The observed Lorentzian lineshape seems to support the latter interpretation.

1. F.Drissler, F.Graf, D.Haarer: J. Chem. Phys. **72**, 4996 (1980)
2. D.Haarer, J.Friedrich: J. Opt. Soc. Am. **70**, 584 (1980)
3. J.Friedrich, J.D.Swalen, D.Haarer: J. Chem. Phys. **71**, 705 (1980)
4. F.G.Pattersen, H.W.H.Lee, R.W.Olson, M.D.Fayer: Chem. Phys. Lett. **84**, 59 (1981)
5. P.W.Andersen, B.J.Halperin, C.M.Varma: Philos. Mag. **25**, 1 (1972)
6. S.K.Lyo, R.Orbach: Phys. Rev. B **22**, 4223 (1980)

Photochemical Hole-Burning at GaAlAs Laser Wavelengths

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The discovery of persistent photochemical hole-burning (PHB) in the zero-phonon lines (ZPL's) of F_3^+ and N_1 centers in NaF [1] established color centers as possible candidates for frequency domain optical storage applications [2]. These ZPL's absorb in the visible, however, and can only be studied with tunable dye lasers. Possible future applications of these systems rest on the demonstration of PHB at GaAlAs laser wavelengths (8000–8500 A). Using a tunable ir dye laser for convenience, we have studied the R_2' center in LiF at 8330 A and have observed narrow, persistent holes in the inhomogeneously broadened ZPL absorption. This represents an important step toward future frequency domain optical storage applications of PHB. Moreover, the hole lineshape is asymmetric, a property which has not been observed for other classes of hole-burning systems. Thus, hole-burning in the R_2' system is of scientific interest as well.

The samples used in these experiments were cleaved from Czochralski-grown boules of LiF doped with Mg^{++} ions. The samples were colored by Mo x-irradiation for 24–48 h at room temperature. Holes were burned and recorded at 2 K using an actively stabilized LD700 dye laser (1 MHz linewidth) with a Kr^+ ion pump. Holes were detected either by observing the fluorescence from the phonon sideband or by using the methods of FM spectroscopy [3].

Holes corresponding to relative absorption changes of as much as 10% can be burned in the R_2' ZPL in 10 s with as little as $100\,\mathrm{mW/cm}^2$ of infrared radiation. The holes decay very slowly in the dark with a time constant on the order of 100 min. The most striking feature of the hole spectrum is the occurrence of two side holes to lower frequency from the burning laser, and one very weak side hole to higher frequency. The central hole and side holes have linewidths on the order of 300 MHz, and the splittings between the various holes are all roughly 1 GHz. The hole spectrum is clearly not symmetric about the burning frequency.

Side holes have not been previously observed for color centers, but they are not uncommon for hole-burning in hyperfine levels [4], for instance. Side holes merely signify the existence of excited state splittings. All previous observations of side holes, however, have yielded symmetric spectra, because hole-burning occurs equally well for all the excited state sublevels in resonance with the laser at various locations in the sample. The asymmetric spectrum observed here can only indicate that the hole-burning process is not equally efficient for each of the excited state sublevels.

In conclusion, PHB at GaAlAs laser wavelengths has been observed for the first time for the ZPL of R_2' centers in LiF. Apart from the practical interest in such a system, the occurrence of an asymmetric hole spectrum indicates that a novel mechanism is responsible for the hole formation.

1. R.M.Macfarlane, R.M.Shelby: Phys. Rev. Lett. **42**, 788 (1979)
M.D.Levenson, R.M.Macfarlane, R.M.Shelby: Phys. Rev. B **22**, 4915 (1980)
2. C.Ortiz, R.M.Macfarlane, R.M.Shelby, W.Lenth, G.C.Bjorklund: Appl. Phys. **25**, 87 (1981)
3. G.C.Bjorklund: Opt. Lett. **5**, 15 (1980)
4. R.M.Macfarlane, R.M.Shelby, A.Z.Genack, D.A.Weitz: Opt. Lett. **5**, 462 (1980)

Persistent Nonphotochemical Hole-Burning of a Molecular Vibrational Mode in Alkali Halide Lattices

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We report the first observation of persistent nonphotochemical hole-burning (NPHB) in the inhomogeneously broadened infrared vibrational mode of a tetrahedral molecular impurity in a crystalline lattice. The transition of interest is the ν_3 mode of ReO_4^- molecules substitutionally doped into alkali halide crystals. Previously, NPHB in a vibrational absorption has only been observed for a low-symmetry molecule in an amorphous Ar matrix [1]. The fact that persistent NPHB even occurs for a tetrahedral molecule at a cubic lattice site focuses attention on the most basic requirements for the occurrence of NPHB effects. Furthermore, the ReO_4^- system features faster burning rates than a number of other hole-burning systems. This makes the study of the mechanism for NPHB in the ReO_4^- system important for possible future device applications.

The samples for this study were annealed, Czochralski-grown crystals of KI or RbI that were doped by the addition of solid $KReO_4$ to the melt. CO_2 and lead salt diode lasers were used to measure the hole growth and erasing dynamics at intensities far below the saturation intensity, I_s ($\simeq$1–3 W/cm^2 [2]). The holes were produced at liquid helium temperatures and were detected in absorption.

The hole lineshape consists of a single, narrow hole, roughly 10 MHz wide, in the inhomogeneously broadened (1–2 cm^{-1} wide) ν_3 mode absorption line. The holes do not decay in amplitude after at least 10 min in the dark at 1.4 K. (Longer dark times were not studied due to laser frequency drift.) The hole growth is neither exponential nor algebraic in time, and appears to be characterized by a continuously changing rate which is fast at small times and slow at large times. The effective hole growth rate is linear in laser intensity over a broad range, indicating that a one-photon process is dominant. The hole depths depend linearly on the ReO_4^- concentration, implying that single molecules are involved in the hole-burning process. The holes may be erased by thermal annealing at temperatures greater than 10 K, or by the application of a second laser beam displaced 10–15 MHz from the hole.

The burning efficiency may be defined as the number of centers losing absorption at the laser frequency divided by the number of photons required to produce this change. For the ReO_4^--alkali halide system, the initial efficiency is approximately 5×10^{-4}. This value is several orders of magnitude larger than the 10^{-6} to 10^{-7} efficiencies observed for photochemical hole-burning in color center systems [3].

Since the observed holes are persistent (i.e., they last much longer than the excited state lifetime $T_1 \simeq 15$ ns [2]), a ground state optical pumping process must be responsible for the hole formation. The two orientations of a tetrahedral molecule at a site of O_h symmetry can give rise to a split, non-relaxing ground state if crystalline strains destroy the equivalence of the two orientations. The vibrational ground state can then be approximated as an asymmetric double well with a central barrier produced by steric effects and a well asymmetry produced by crystalline strains. In fact, a phenomenological photon-induced reorientation model based on the assumption of two absorption frequencies for each center accounts for most of the observed data. Moreover, the asymmetric double well model is supported by the experimental observation of deeper holes in the wings of the inhomogeneously broadened line.

To conclude, these studies of the ReO_4^--alkali halide system illustrate that NPHB can occur for a high symmetry molecule at a cubic site if crystalline strains disturb the equivalence of the various molecular orientations. The long hole lifetime and fast burning rate indicate that the barrier to reorientation is very high in the vibrational ground state and much lower in the vibrational excited state, respectively.

1. M.Dubs, H.H.Gunthard: Chem. Phys. Lett. **64**, 105 (1979)
2. W.E.Moerner, A.J.Sievers, A.R.Chraplyvy: Phys. Rev. Lett. **47**, 1082 (1981)
3. G.C.Bjorklund: Private communication

Investigation of Gas Surface Interaction by Laser-Induced Fluorescence: Scattering of NO Molecules on Graphite

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An important aim in research on catalysis is the understanding of the gas-surface reaction dynamics and the knowledge about the underlying interaction potential between gaseous particles and surface atoms. Scattering atomic and molecular beams on well-defined surfaces and measuring angular and velocity distributions is a powerful tool to elucidate the elementary interaction steps.

Recently, the method of laser-induced fluorescence has been successfully applied to obtain additional information on the surface scattering process. The probing of incoming and scattered molecules by laser light can yield their internal energy distributions [1–4]. This knowledge helps to understand the energy transfer mechanism between the impinging molecule and the surface. Simultaneously, inelastic events like the intramolecular transformation of translational to rotational modes during the interaction process can be studied.

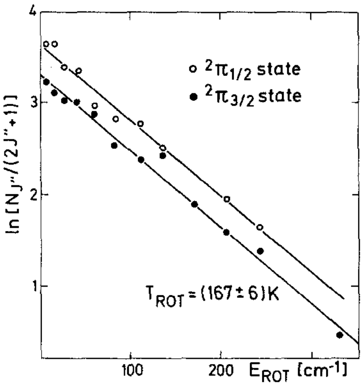

Fig. 1. Plot of $\ln[N_{J''}/(2J''+1)]$ versus $J''(J''+1)$ showing Boltzmann-type rotational distributions of both the $^2\pi_{1/2}$ and the $^2\pi_{3/2}$ ground state of NO molecules scattered on a graphite surface at 170 K

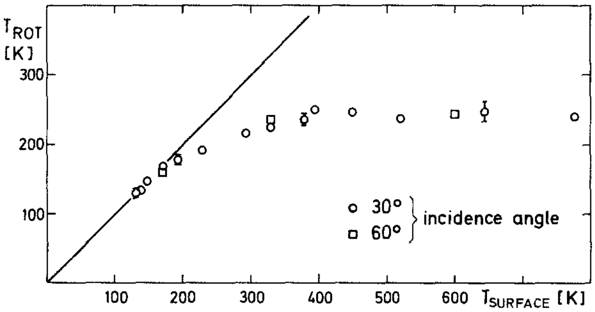

Fig. 2. Rotational temperature of scattered NO molecules versus the temperature of the graphite surface at different incidence angles

In the described experiment the internal state distribution in the ground state doublet of rotationally cold (38 K) NO beam molecules scattered on a graphite single crystal was investigated. The angular distribution of the outgoing molecules showed a lobular peak of particles scattered in specular direction as well as molecules scattered according to the cosine law. These two regimes can be attributed to a weakly inelastic event and to a trapping-desorption process. The number of specularly scattered molecules remained constant at surface temperatures above 370 K and began to decrease when the sample temperature was lowered.

By changing the angle of incidence of the molecules the particles of the two scattering regimes were investigated by laser-induced fluorescence at different sample temperatures.

The rotational population distributions of the scattered molecules could be described by Boltzmann-type distributions; both substates $^2\pi_{1/2}$ and $^2\pi_{3/2}$ showed the same rotational temperature. Comparing the overall population of the two sublevels which are spaced by the spin-orbit energy of 123 cm^{-1} one finds a Boltzmann equilibrium characterized by the same temperature as the rotational energy levels. The results suggest comparable rates for the rotational relaxation as well as for the relaxation between the fine structure levels. As the residence time in the gas-surface interaction potential for a weakly inelastic encounter can be assumed in the range of 10^{-11} s, this gives an upper limit for the relaxation time.

The measured rotational temperatures indicate full rotational accommodation for a crystal temperature range up to about 150 K. For higher surface temperatures the rotational temperature begins to deviate from the line of full accommodation to lower values. Increasing the crystal temperature above 370 K results in a constant value for T_{rot} of about 250 K. No difference in rotational temperature could be detected whether probing specularly reflected particles or molecules scattered in a cosine distribution.

In combination with the angular distribution measurements these results enable us to describe the interaction mechanism as a transition between two scattering regimes. At high surface temperatures scattering is dominated by weakly inelastic encounters. For this case the limiting factor for the energy transfer into internal modes seems to be the total beam energy (in our case about 720 cm^{-1}). Decreasing the crystal temperature causes a higher residence time for the scattered molecules in the interaction potential leading to a more efficient coupling to the surface modes.

1. F.Frenkel, J.Häger, W.Krieger, H.Walther, C.T.Campbell, G.Ertl, H.Kuipers, J.Segner: Phys. Rev. Lett. **46**, 152 (1981)
2. G.M.McClelland, G.D.Kubiak, H.G.Rennagel, R.N.Zare: Phys. Rev. Lett. **46**, 831 (1981)
3. A.W.Kleyn, A.C.Luntz, D.J.Auerbach: Phys. Rev. Lett. **47**, 1169 (1981)
4. J.W.Hepburn, F.J.Northrup, G.L.Ogram, J.C.Polanyi, J.M.Williamson: Phys. Lett. (in press, 1982)

Laser-Induced Decomposition of Organometallic Compounds

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The organometallic compounds can be used for preparation of conductive and resistive layers in the electronics. Because of the weak bond between the metal ion and the organic radical the organometallic compounds (OMC) decompose at relatively low temperatures, T_d (about 300 °C). By the OMC decomposition in solid phase thin metal layers of specific electrical properties build up. The use of OMC in the electronics may become very effective if a laser is used as a heat source, making possible the localization of the chemical reaction in the zone of laser radiation action only.

In this paper the experimental results of the investigation of laser-induced decomposition of $Cu(HCOO)_2$ are presented. This OMC has been previously deposited on the surface of various dielectric substrates in the form of $\sim 100\,\mu m$ thick paste layer, prepared from mixture of OMC, glass powder and organic bonding substance in percentage ratio 100:5:20. In the experiments for the decomposition of $Cu(HCOO)_2$ a Nd : glass laser, operating in free generation regime with pulse duration $\tau^p = 1$ ms and pulse energy up to 20 J, as well as cw CO_2 and Nd : YAG lasers with mean power up to 10 W, have been used. In the case of cw laser radiation the effective time, τ, of the laser action has been determined as $\tau = l_0/U$ (l_0 is the dimension of the zone of laser radiation action, U is the sample motion velocity relatively the laser beam). The resistance of the metal layer, formed after the decomposition of $Cu(HCOO)_2$, has been measured by a Wheatstone bridge.

By the thermal laser radiation action the OMC decompose in pure copper and volatile components:

$$Cu(HCOO)_2 \xrightarrow{T_d} Cu\downarrow + H_2O\uparrow + CO\uparrow + CO_2\uparrow .$$

The thickness of the Cu film, built up by the laser-induced decomposition of $Cu(HCOO)_2$ has been evaluated qualitatively measuring the specific surface resistance, $R_\square$, of the film $R_\square = \varrho/h$ (ϱ is the film density, h is the thickness of the film).

The dependence of $R_\square$ and h on the effective time of action, τ, of a cw laser radiation is presented in Fig. 1. One can see that with the increase of τ, $R_\square$ drops and h increases, which is due to the more effective flow of the chemical reaction. With the decrease of τ, $R_\square$ increases and h decreases, and at $\tau < \tau_{th}$ (τ_{th} is a threshold value of τ) the decomposition process stops.

The results in Fig. 1 are obtained, using cw laser radiation of power $P = 0.6$ W, which corresponds for a 200 µm zone of action to light flux density $Q = 1.35 \times 10^3$ W cm^{-2}. With the increase of P the curves in Fig. 1 shift to the left. $\tau = 1$ ms corresponds to $Q = 1.3 \times 10^3$ W cm^{-2}, which is approximately equal to the threshold value, Q_{th}, of Q for pulsed laser radiation from Nd : glass laser ($\tau^p = 1$ ms).

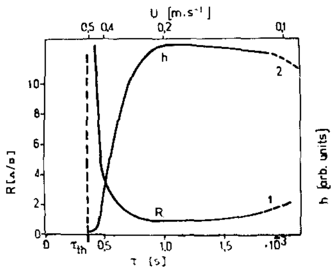

Fig. 1

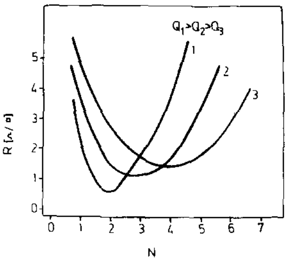

Fig. 2

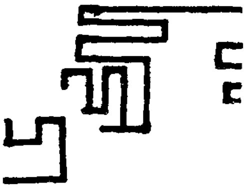

Fig. 3

In Fig. 2 the dependence of $R_\square$ on the laser pulses number, N, at various light flux densities Q is presented. This dependence has an analogous character as by a multiple action of cw laser radiation. By multiple laser radiation action a dense and well conductive layer of Cu builds up. As one can see from Fig. 2 the OMC decomposition takes place in the first several laser pulses. Than the formation of uninterrupted metal layer and its thermal treatment take place. In this stage the resistance of the layer drops to minimum value. Further increase of N leads to increase of $R_\square$ due to oxidation of the layer and to its partial evaporation.

The process of laser-induced decomposition of $Cu(HCOO)_2$ has been used to prepare conductive tracks on the surface of dielectric substrates. The unirradiated zones of the OMC layer have been washed away by a suitable solvent, while the metallized irradiated zones remained on the substrate (Fig. 3 – the black lines are metallic).

Laser-induced decomposition of $W(CO)_4$ and $Mo(CO)_4$ has also been experimentally realized. In result resistive layers of W and Mo with $R_\square \sim 200\,\Omega/\square$ have been obtained.

Generation of Surface Microstructure in Metals and Semiconductors by Short Pulse CO_2 Lasers

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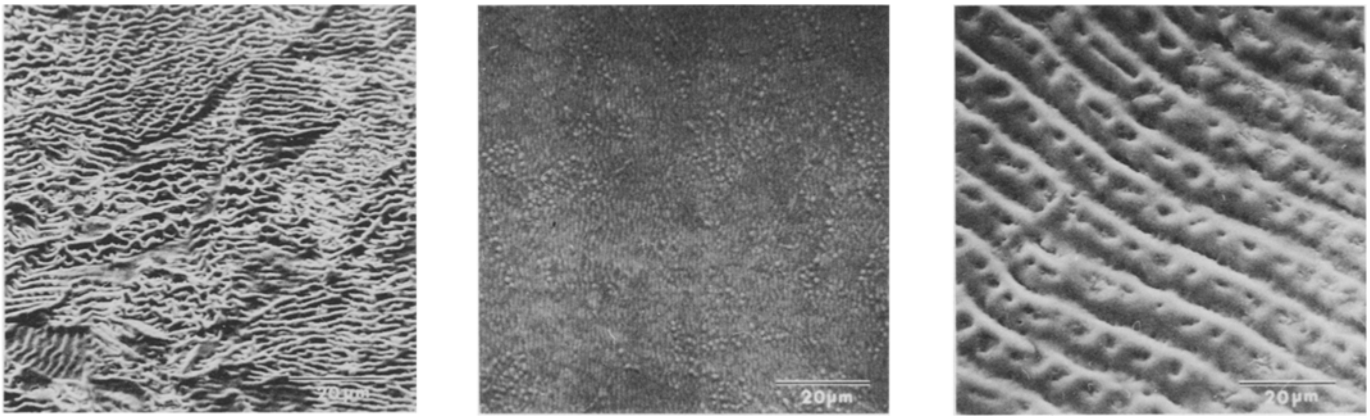
Interaction of laser radiation with material surfaces has been extensively studied over the past ten years. Most of this work has concentrated on laser energy regimes where permanent surface modifications occurred (e.g., damage) or where controlled surface/impurity changes occurred (e.g., annealing). In this report we shall concentrate on the boundary between the two regions where the laser fluence is high enough to cause permanent and quite dramatic changes in the material surface but where the fluence is below the conventionally defined damage threshold.

In these experimental tests, a 1.7-ns CO_2 laser is used to irradiate surfaces of metals and semiconductors at fluence levels up to $10\,\mathrm{J/cm^2}$. Laser fluence is carefully controlled so that variations in the peak on-axis brightness are less than $\pm 5\%$. The input fluences F, are adjusted to a value less than the experimentally determined single-shot damage fluence F_0 (typically $F/F_0 \sim 0.90$ are used) and the surface is then irradiated with a sequence of laser pulses. We shall describe the complex modification of the surfaces that occurs during these irradiation sequences as determined by the measurements of the optical properties of the surface during the test sequences and post-testing examination using scanning electron micrographs. In general the polished or micromachined surfaces develop a fine-scale linear surface microstructure that evolves into a spherical structure at longer laser irradiation sequences. Figure 1 shows the linear stage of the surface development for several materials tested. In all cases the input fluence is below the measured one-shot damage fluences.

Several theories have been proposed to explain similar behavior observed in semiconductors [1] and dielectrics [2]. We shall compare our current results to these earlier works and show that a partial explanation of the linear growth phase observed in the present experiments is consistent with these earlier works. The spherical growth phase has not been observed before and is not predicted by the current theories.

Finally we shall discuss the practical implications of these observations to the lifetime and lifetime criteria as applied to optical components used in high-energy or high-average power laser systems and will suggest a better and more quantifiable definition of laser damage based on the actual performance requirements of the optical element.

1. G.N.Maracas, G.L.Harris, C.A.Lee, R.A.McFarlane: Appl. Phys. Lett. **33**, 453 (1978)
2. P.A.Temple, M.J.Soileau: IEEE J. QE-**17**, 2067 (1981)



Copper (20 Shots) Molybdenum (40 Shots) Silicon (100 Shots)

Fig. 1. $F/F_0 = 0.88$–1.7 ns at 10*P*20 CO_2 (SEM – × 1000)

Laser Induced Chemical Vapor Decomposition of C and Si

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Laser induced chemical vapor deposition (LCVD) may become an interesting method for direct generation of material patterns. The deposition process can be achieved either by photolytical [1] or by pyrolytical [2, 3] decomposition of molecules from the gas phase.

In this paper we report on LCVD by using the visible radiation of an Ar^+ laser for local substrate heating. Detailed experiments on the deposition of C from C_2H_2, C_2H_4, and CH_4 [2, 3], and of Si from SiH_4 [4] were performed. Two types of samples were grown: layers in the form of stripes and cylindrical rods (Fig. 1). Stripes with widths down to 5 µm were produced. The polycrystalline nature of the deposited material was established by Debye-Scherrer x-ray diffraction and by Raman scattering experiments.

Quantitative investigations of the temperature dependence of the deposition rate were exclusively performed during the steady growth of the cylindrical rods. In this phase of growth the lateral extension of the rod remains constant, and the surface temperature, $T_s(r)$, depends only on the laser irradiance, and on the

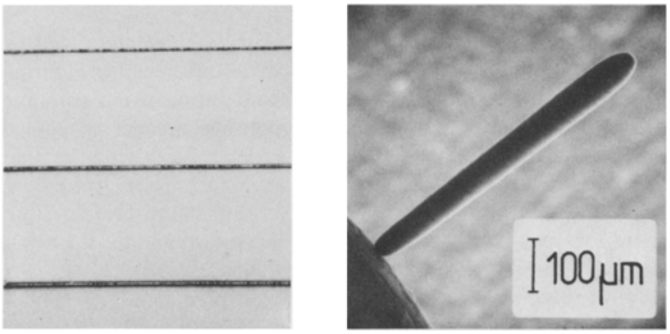

Fig. 1. Left side: Stripes of polycrystalline C produced with different laser irradiances but constant scanning velocity. Right side: Carbon rod grown with 2260 W/mm^2 on tungsten wire

reflectivity, the thermal conductivity, and the geometry of the deposited material. Because of the Gaussian shape of the laser beam, $T_s(r)$ shows its maximum value near the rod axis, i.e. at $r=0$, and decreases continuously to the edge. From an analysis of the growth mechanisms [3], it follows that the lateral growth velocity vanishes at $r=0$. Therefore, the axial growth velocity is equal to the overall growth in length, and we define the deposition rate by $v(r=0, T_s) \equiv w(T) = dl/dt$. With the experimental setup described in [3], the parameters w and T could be measured simultaneously.

Figure 2 shows an Arrhenius plot of the deposition rate of C for various pressures of C_2H_2. The error bars represent the standard error evaluated from a great number of single data points.

Two qualitatively different temperature regimes are observed: The linear regime reflects an exponential increase of the deposition rate with temperature. From the slope of the dashed line, which is a least squares fit through the data points in this regime, an apparent activation energy of 47 ± 2 kcal/mol was derived. Within accuracy of measurements, this value is constant within the range of pressures covered by the experiments. In corresponding measurements for the deposition of Si from SiH_4 the linear regime reaches up to about 1400 K ($p_{SiH_4} = 133$ mbar); the activation energy is 44 ± 4 kcal/mol, and the deposition rates are of the same order of magnitude. The observed activation energies are within the range of values reported for heterogeneous and homogeneous [5] decomposition of carbon and silane. Therefore, in the "low" temperature regime the LCVD of carbon and silane seems to be kinetically controlled. The enormous deposition rates, which are two to three orders of magnitude higher than those reported for conventional CVD processes, may be explained by the much higher gas pressures which can be used in the LCVD experiments.

A further interesting feature in Fig. 2 is the marked decrease in slope above a certain temperature. This change in slope may indicate that the deposition becomes limited by transport [3]. However, we cannot yet rule out that the decrease in slope is also influenced by the possible onset of particle formation or by different pathways in chemical reactions.

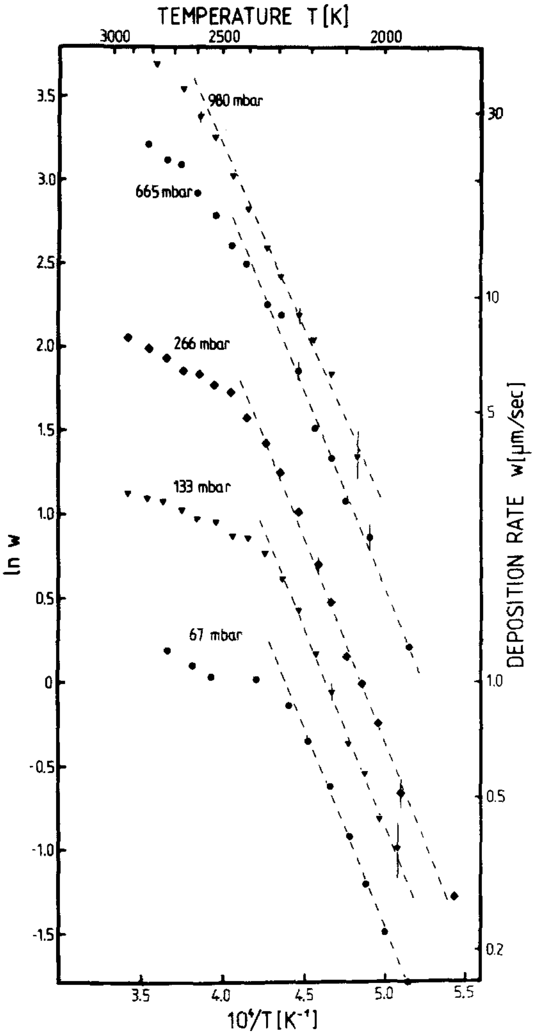

Fig. 2. Arrhenius plot for laser induced deposition of C from C_2H_2. Slopes of dashed lines correspond to 47 ± 2 kcal/mol

1. D.J.Ehrlich, R.M.Osgood, T.F.Deutsch: IEEE J. QE-**16**, 1233 (1980)
2, 3. G.Leyendecker, D.Bäuerle, P.Geittner, H.Lydtin: Appl. Phys. Lett. **39**, 921 (1981); (in press, 1982)
4. D.Bäuerle, P.Irsigler, G.Leyendecker, H.Noll, D.Wagner: Appl. Phys. Lett. (in press, 1982)
5. See e.g. J.Bloem, L.J.Giling: Current Topics in Materials Science, Vol. 1, ed. by E.Kaldis (North-Holland, Amsterdam 1978) p. 147