Photochemical dry etching of GaAs

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sprayed under various conditions. The absorption edges of layers sprayed from $CuCl_2$ are uniformly sharper than those of films sprayed from either neutralized or non-neutralized CuCl solutions. These data are further evidence of the improvement in film quality which occurs when $CuCl_2$ is used as the Cu source. Further analysis of these data is in progress.

A p-CuInSe$_2$/n-CdS junction was prepared by evaporating CdS onto one of the double-layer CuInSe$_2$ films on glass. This cell suffered from large series resistance, as was expected, which severely degraded fill factor and short circuit current. However, after a 40-min heat treatment in air at 200 °C, the open circuit voltage was 0.558 V (AM1.5). This is the highest V_{oc} ever reported for a polycrystalline CuInSe$_2$/CdS cell, and is very close to the V_{oc} of 0.56 V obtained from cells prepared with single crystal CuInSe$_2$.[1] This is another indication of the quality of CuInSe$_2$ produced when $CuCl_2$ is used in the spray solution. Attempts to reduce the series resistance without introducing shorting paths are in progress.

[1] J. L. Shay, S. Wagner, and H. M. Kasper, Appl. Phys. Lett. 27, 89 (1975).
[2] Y. R. Hsiao, W. S. Chen, R. A. Mickelsen, J. M. Stewart, V. Lowe, L. C. Olsen, and A. Rothwart, Final Report, May 14, 1982–May 13, 1983, Solar Energy Research Institute contract XE-2-02038-1.
[3] L. L. Kazmerski, M. Hallerdt, P. J. Ireland, R. A. Mickelsen, and W. S. Chen, J. Vac. Sci. Technol. A 1, 395 (1983).
[4] C. W. Bates, Jr., K. F. Nelson, S. A. Raza, J. B. Mooney, J. M. Recktenwald, L. MacIntosh, and R. Lamoreauxe, Thin Solid Films 88, 279 (1982).
[5] C. R. Abernathy, C. W. Bates, Jr., A. A. Anani, and B. Haba, Thin Solid Films 115, L41 (1984).
[6] J. B. Mooney, R. H. Lamoreaux, and C. W. Bates, Jr., Final Report, 1 June 1982–30 November 1983, Solar Energy Research Institute contract XL-2-02115-01.
[7] C. W. Bates, Jr., M. Uekita, K. F. Nelson, C. R. Abernathy, and J. B. Mooney, Appl. Phys. Lett. 43, 851 (1983).
[8] J. Parkes, R. D. Tomlinson, and M. J. Hampshire, J. Appl. Cryst. 6, 414 (1973).
[9] R. W. Birkmire, R. B. Hall, and J. E. Phillips, Final Report, March 16, 1982–March 15, 1983, Solar Energy Research Institute contract XL-2-02078-01.
[10] J. Pankove, Optical Processes in Semiconductors (Prentice–Hall, New York, 1971).

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GaAs exhibits greatly enhanced reactivity with gas-phase reactive Cl species when the surface is irradiated with low intensity laser light having a frequency which can excite above the band gap of GaAs. This laser-induced reactivity is shown to be photochemical rather than thermal in origin. This is the first reported observation of a purely photochemical dry etching process for a III-V semiconductor material.

There are two principal mechanisms whereby laser irradiation of a GaAs surface might facilitate reaction of GaAs with reactive Cl species such as Cl atoms and negative ions. The first is a purely thermal process. Since the laser heats the GaAs surface in the region of light absorption, a local increase in the temperature of the GaAs surface may increase the local etching rate for a thermally activated chemical reaction or may lead to laser-assisted vaporization of reaction products or of original sample material. Laser-enhanced thermal etching employing high intensity radiation has been reported previously and thermal mechanisms have been proposed to explain the observed etching behavior.[1-3] However, the etched holes produced in these thermal dry etching studies were irregular in shape[1] or exhibited excessive roughness.[2,3] Similar photothermal effects have been observed for etching of Si[4] and Ge.[5] In addition, thermal etching processes would not be expected to exhibit much reaction selectivity. The second mechanism is photochemical rather than thermal in nature. Production of electron-hole pairs due to light absorption in the surface region of GaAs may open an alternative photochemical reaction pathway to that of the thermal reaction. Due to the inherent selectivity of photochemical reactions, photochemical dry etching processes may offer distinct advantages over thermal processes for selective etching requirements. Enhancement of etching of Si by F due to a photochemical process has been reported under conditions where the thermal etch rate is comparable to the photochemical etch rate.[6,7] We have identified and studied the laser-induced etching of GaAs by reactive Cl species. All evidence from this study indicates a purely photochemical mechanism is responsible for the observed increase in reaction under low-intensity laser irradiation. This is the first time a purely photochemical dry etching process for a III-V semiconductor material has been observed.
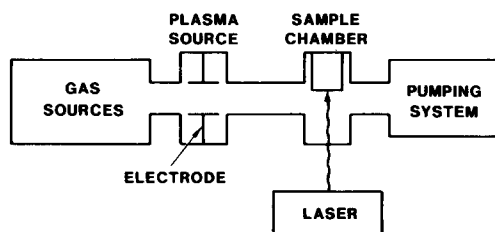
FIG. 1. Diagram of experimental apparatus.

FIG. 2. Profile of a photoetched hole in p-GaAs produced at a laser power of 0.18 W.

A schematic diagram of the apparatus employed in this study is presented in Fig. 1. The samples were GaAs (100) from Crystal Specialties, Inc. No pretreatment to remove native oxide was employed. Carrier concentrations of $4.5 \times 10^{17}/cm^3$ and $7 \times 10^{17}/cm^3$ were measured for the Si-doped n-GaAs and Zn-doped p-GaAs, respectively. Reactions were run at a sample temperature of 370 K, unless otherwise specified, to facilitate evaporation of reaction products.[8,9] The gas-phase Cl reactants were generated in a dc plasma located 10 cm upstream from the sample. The plasma electrodes were 316 stainless steel discs of 2.5 cm diameter separated by 1.0 cm. Voltage between the discs was -370 ± 5 V, with an interelectrode current of 0.6 mA. Since moderate concentrations of Cl radicals and ions will etch GaAS in the absence of light,[9] the Cl species concentrations were reduced to a level where no etching was detectable with a Dek tak profilometer in the absence of light of energy greater than the band gap of GaAs. This was achieved by dilution of HCl with He since a minimum pressure of nearly 1 Torr was required to sustain a glow discharge. The gas mixture employed was 3.00 Torr He with 0.11 Torr of 5% HCl in He. The He flow rate was 510 sccm, which corresponds to a mean velocity of 250 cm/s. Reactions were run for 1800 s. Although actual Cl species concentrations were not measured directly, the same pressure and plasma conditions were used for all runs to ensure the same supply of Cl reactants and, consequently, self-consistent reaction conditions for all measured etch rates.

The photon source was a focused Ar^+ laser operated at 514.5 nm in the TEM_{00} mode. The beam dimensions were measured with a Reticon photodiode array with 25-μm resolution. The array was located at a position in the optical setup which corresponded to the sample surface. The beam was Gaussian with full width at half-maximum $= 150 \pm 25$ μm. The laser power was set at a constant value and the power on the sample surface was varied by insertion of neutral density filters into the optical path. Laser power at the sample surface was varied from 0.056 to 0.22 W.

Etch profiles were measured with a Dek tak profilometer. Etch rates were defined by the maximum etch depth measured at beam center for a 1800-s reaction. These rates do not represent the maximum rate possible, since no attempt was made to optimize reaction conditions.

A typical etch profile is presented in Fig. 2. A smooth Gaussian-shaped hole which replicates the laser beam profile is etched in the GaAs sample. No smoothing routines were used to produce this figure; extremely smooth holes are produced by this photoetching technique. This contrasts sharply with the rough holes produced by laser-assisted thermal etching.[2,3] The etch depths produced by varying laser
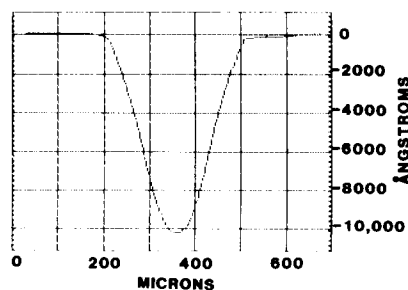
power are presented in Fig. 3 for both p-GaAs and n-GaAs. For both dopant types, etch depth increases linearly with laser power. For a constant laser power, etch depth increases linearly with time with an intercept at zero, indicating that the initial presence of the thin layer of native oxide does not inhibit the photoreaction to any significant extent.

One would expect a purely photochemical reaction to exhibit the linearity in laser power illustrated in Fig. 3 since the number of electron-hole pairs produced is proportional to the photon flux, which is determined by the laser power for constant beam dimensions. One would also expect to observe a dependence on laser power for a purely thermal reaction. However, this dependence in the thermal case would not be linear but, rather, would depend exponentially on the temperature rise induced at the GaAs surface for a given laser power. One may calculate the temperature rise at the surface of a material induced by a Gaussian laser beam of known profile and power.[10] Neglecting power losses due to reflectance at the GaAs surface, the maximum calculated temperature rise at beam center for a laser power of 0.22 W is 26°, while a laser power of 0.056 W produces a maximum rise of 7°. An Arrhenius plot of the natural log of the experimental etch depths at beam center versus the reciprocal temperature of the sample is presented in Fig. 4. The two sets of data points represented the difference in temperature calculated assuming a reflectance of 0.0 or 0.39.[11] The actual temperature of the samples should lie somewhere between these extremes. However, it is clear that marked curvature is present regardless of the actual value of the reflectance. Therefore, the Arrhenius behavior expected of a thermal process is ab-
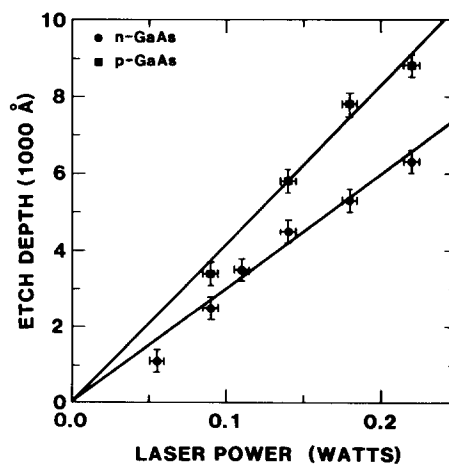

FIG. 3. Etch depth at beam center vs laser power for n-GaAs ($4.5 \times 10^{17}/cm^3$) and p-GaAs ($7 \times 10^{17}/cm^3$).
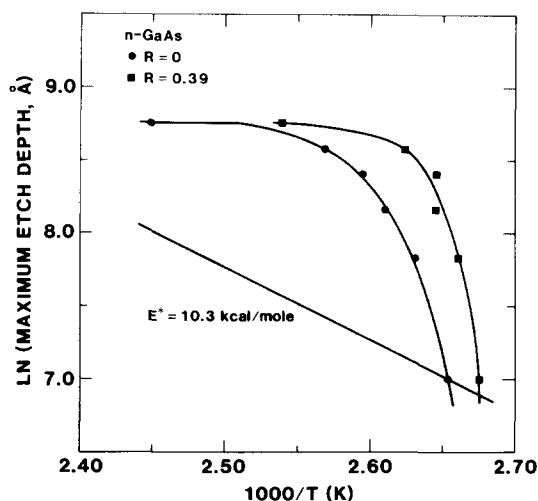
FIG. 4. Arrhenius plot of etch depths for n-GaAs for sample temperatures calculated assuming a reflectance of 0 (circles) or 0.39 (squares). Actual sample temperature should lie between these extremes. The straight line indicates the expected behavior for an activation energy of 10.3 kcal/mole, as measured for the corresponding thermal reaction.

sent in this photoinduced reaction. A study of the temperature dependence of the thermal reaction in a planar plasma reactor using Cl_2 as the source of reactive Cl species showed Arrhenius behavior over the temperature range from 490 to 580 K with an experimental activation energy of 10.3 kcal/mole.[12] The straight solid line in Fig. 4 illustrates the expected temperature dependence of the etch depth if the laser were only increasing the thermal reaction rate. The lack of fit to the experimental etch depths is clear evidence of the existence of a nonthermal reaction mechanism. As a further test of the apparent temperature independence of the photoreaction, two samples of n-GaAs with carrier concentration of $1 \times 10^{18}/cm^3$ were heated to 361 and 384 K and reacted under a laser power of 0.18 W, which gives a calculated maximum temperature rise of 21° to 382 and 405 K, respectively. This serves to simulate the calculated maximum temperature range for the samples reacted at different laser powers (377–396 K). The measured etch rates for the samples at 361 and 384 K were 4700 ± 300 Å and 4850 ± 100 Å, respectively. Thus, it is clear that the laser is not increasing the reaction rate of GaAs by merely heating the surface and thereby facilitating a thermally activated reaction. Although such purely photochemical effects have not been observed before in a dry etching process for GaAs, the laser-assisted

formation of GaAs oxide under similar low power density laser radiation also appears to be photochemical rather than thermal in origin.[13,14]

In summary, GaAs exhibits greatly enhanced reactivity with gas-phase Cl species when the surface is irradiated with low-intensity laser light where the photon energy is greater than the band gap of GaAs. The dependence of this reaction on laser power and temperature is inconsistent with a thermal process. Rather, the creation of electron/hole pairs by laser irradiation induces a truly photochemical reaction of GaAs with the reactive gas-phase Cl species. This is the first reported observation of a purely photochemical dry etching process in a III-V semiconductor material. Further studies to identify the mechanism of this photochemical reaction are in progress.

[1]A. W. Tucker and M. Birnbaum, Proc. Soc. Photo-optical Instrum. 385, 131 (1983).
[2]M. Takai, J. Tokuda, H. Nakai, K. Gamo, and S. Namba, Jpn. J. Appl. Phys. 22, L757 (1983).
[3]N. Tsukada, S. Semura, H. Saito, S. Sugata, K. Asakawa, and Y. Mita, J. Appl. Phys. 55, 3417 (1984).
[4]D. J. Erlich, R. M. Osgood, Jr., and T. F. Deutsch, Appl. Phys. Lett. 38, 1018 (1981).
[5]G. P. Davis, C. A. Moore, and R. A. Gottscho, Proc. Soc. Photo-optical Instrum. Eng. 459, 115 (1984).
[6]F. A. Houle, J. Chem. Phys. 79, 4237 (1983).
[7]P. Brewer, W. Holber, G. Reksten, and R. M. Osgood, Jr., Proc. Soc. Photo-optical Instrum. Eng. 459, 128 (1984).
[8]G. Smolinsky, R. P. Chang, and T. M. Mayer, J. Vac. Sci. Technol. 18, 12 (1981).
[9]R. H. Burton and G. Smolinsky, J. Electrochem. Soc. 129, 1599 (1982).
[10]M. Lax, J. Appl. Phys. 48, 3919 (1977).
[11]B. O. Seraphin and H. E. Bennett, in Semiconductors and Semimetals, edited by R. K. Willardson and A. C. Beer (Academic, New York, 1967), Vol. 3, p. 523.
[12]V. M. Donnelly, D. L. Flamm, C. W. Tu, and D. E. Ibbotson, J. Electrochem. Soc. 129, 2533 (1982).
[13]S. A. Schafer and S. A. Lyon, J. Vac. Sc. Technol. 19, 494 (1981).
[14]W. G. Petro, I. Hino, S. Eglash, I. Lindau, C. Y. Su, and W. E. Spicer, J. Vac. Sci. Technol. 21, 405 (1982).