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# Laser-induced homoepitaxy of GaP

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Laser-induced pyrolytic process is utilized to "direct write" epitaxial GaP structures. The precursors used were trimethylgallium and tertiarybutylphosphine, a new phosphorus donor. Dependence of the epitaxial growth on several deposition parameters is examined.

Laser-induced reactions have been successfully used for deposition of a wide range of materials.[1] An important attribute of this process is the high spatial resolution deposition that can be achieved without the use of photolithography. We describe below the application of this technique for epitaxial growth of GaP microstructures for potential optoelectronic applications.

Recently, several groups have reported deposition of epitaxial III-V compound semiconductors using either laser-induced photolytic[2,3] or pyrolytic[4–7] reactions. These reactions are characterized by the laser wavelength and the absorption spectra of the reactant gases and the substrates. The latter process was employed for this investigation where the heating of the substrates was confined over very small lateral dimensions. The objective of the investigation reported here was to examine some of the deposition parameters required for selective epitaxial growth of GaP.

The experimental configuration is sketched in Fig. 1. The 514.5 nm output from an argon ion laser first passes through a beam expander and then is steered into a multiple element $f/5.6$ focusing lens. The lens was mounted on a precision $X$-$Y$ stage, which can be translated a maximum of 2 in. along each axis by stepper motors in increments of 0.1 $\mu$m. By programming the motions of the stepping motors it was possible to "write"various geometric patterns. Typically 3-mm-long lines and $500\times500$ $\mu$m pads were grown. A vidicon camera allowed us to visually monitor the location of the deposition and in-process growth. The substrates were placed in a stainless-steel reaction cell which had a quartz window. The cell was designed to accommodate 2-in.-diam substrates. The gas manifold and the deposition cell were heated to about 120 °C to avoid any condensation of the precursor gases, especially on the window. All the depositions reported below were obtained under static gas conditions.

The precursor gases for deposition of GaP were electronic grade trimethylgallium (TMG) and tertiarybutylphosphine (TBP), which is a relatively new phosphorus source. TBP was selected over phosphine due to lower safety risks.[8] Once the cell was filled with appropriate partial pressures of the precursors, its pressure was brought up to one atmosphere with hydrogen. Several different substrates have been examined; however, the discussion here will be limited to GaP. Liquid encapsulated Czochralski (LEC) GaP substrates were used, which were first degreased in organic solvents, followed by a 1 min etch in a 10:1:1 mixture of $H_2SO_4$:$H_2O_2$:$H_2O$. This was followed by a de-ionized water rinse and dry blowing with nitrogen before they were loaded into the deposition cell.

One of the first series of experiments involved examination of the partial pressures of the precursor gases. As expected, the growth rates increased with partial pressures at constant laser conditions. For example, at TMG partial pressure of 12 Torr, V/III ratio of 15, and laser power of 2 W, GaP depositions over 2 $\mu$m thick were obtained with a single scan. These depositions were obtained on several different substrates, including Si and GaAs. However, these deposits proved to be polycrystalline. Obviously the growth rates had to be reduced in order to obtain epitaxial films. This was achieved by reducing the concentrations of the precursors and using low-power, multiple laser scans.

Smooth and continuous epitaxial lines and pads (by raster scanning) were deposited over a range of scan speeds (50–125 $\mu$m/s) and laser power (1–2 W) at TMG partial pressures of 2–4 Torr and a V/III ratio range of 10–20. The growths were stoichiometric over this V/III ratio range. The thickness of the deposits as a function of the number of scans is shown in Fig. 2, where the scan speed was 100 $\mu$m/s, V/III

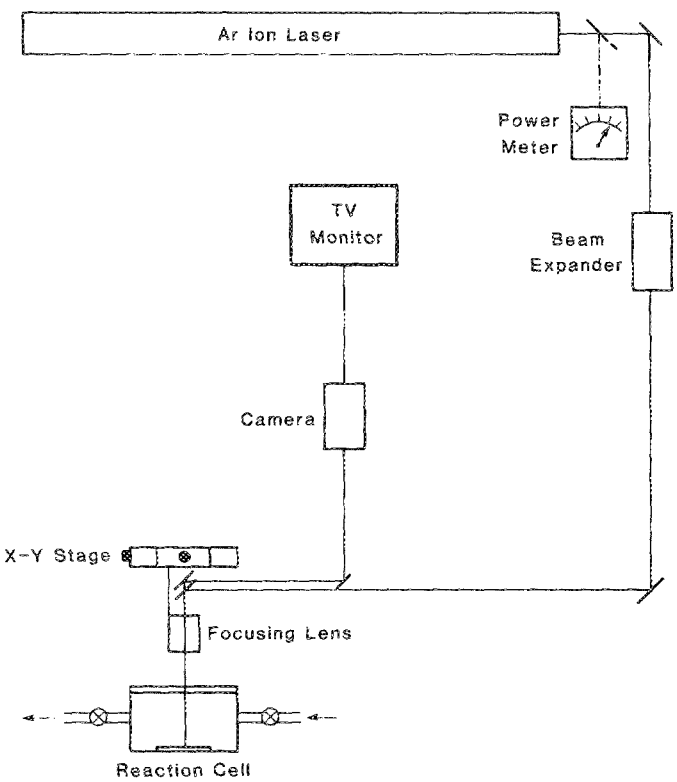


FIG. 1. Schematic diagram of the experimental arrangement.

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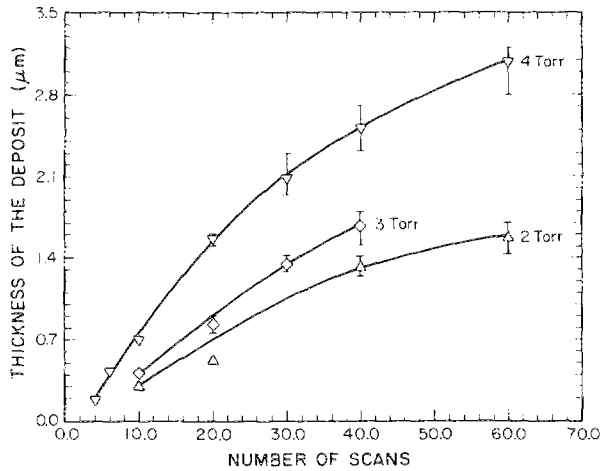


FIG. 2. Epitaxial growth vs the number of scans at 2, 3, and 4 Torr TMG partial pressures.

ratio of 10, and laser power of 1 W. It can be seen that initially the growth per scan is relatively high; however, it gradually decreases. Simple calculations show that the concentration of the reactants was enough to write at least $10^3$ more structures. Therefore, depletion of reactants was not considered to be the reason for leveling off of the growth/scan. We feel one of the reasons for the slowing of the growth is the decrease in laser intensity. This can be visualized by considering the projection of a circular area on the spine of a ridge structure. As the growth progresses, the height of the ridge increases which further increases the projected area on it. This in turn reduces the laser intensity. A simple model based on this premise agrees with the observed trend in growth/scan.

An example of a direct-write structure is shown in Fig. 3, which is a scanning electron micrograph. End view of this structure measures about 6.3 $\mu$m wide at the base and 2.5 $\mu$m high. Gaussian curve fit to profilometer data showed reasonable agreement, especially for the bottom half of the deposit. Top half of the deposit is slightly narrower than the Gaussian profile. The areas under these profiles (calculated by the profilometer) were proportional to their heights. Therefore, the amount of deposition is represented in terms of their heights. An exception to this was at high laser power where double peaks were observed.[9]

The crystalline properties of the direct-write structures were too small to be examined with an x-ray diffractometer available to us, therefore transmission electron microscopy (TEM) was utilized. Cross-sectional samples were prepared using the standard procedure which includes ion milling. Figure 4 shows a typical electron diffraction pattern of the laser deposited GaP, which verifies epitaxial growth. TEM micrographs have also provided interesting information about defects in the substrate and in the epigrowth. For example, a relatively large number of defects are seen in the far wings of the cross-sectional profile. This is probably due to low growth temperatures.

The stoichiometry of the deposition was first examined using energy dispersive x-ray spectroscopy and then Auger electron spectroscopy. Since the phosphorus precursor was organometallic and is not well characterized, our main concern was incorporation of carbon in the deposit. Figure 5 shows a typical Auger spectrum (after 2.5 min Ar sputter) of the laser deposited epitaxial GaP. It can be seen that the incorporation of carbon in the growth is negligible. In this case the Ga and P atomic concentrations were 51.7% and 48.3%, respectively.

Another important growth parameter was found to be the scan speed. Figure 6 shows the dependence of the growth at three different scan speeds. At 50 $\mu$m/s, although the initial growth rate is high, the profile becomes rough and irregular after a large number of scans. As the scan speed was increased, the profiles became smoother. The data in Fig. 6 were obtained at TMG pressure of 4 Torr, V/III ratio of 10, and 1 W laser power. Under these conditions best profiles were obtained at a scan speed of 100 $\mu$m/s. At higher speeds the lines grown are discontinuous.

Other parameters examined included the laser power and the substrate orientation. The epitaxial growth rate initially increases with the laser power and then drops. For

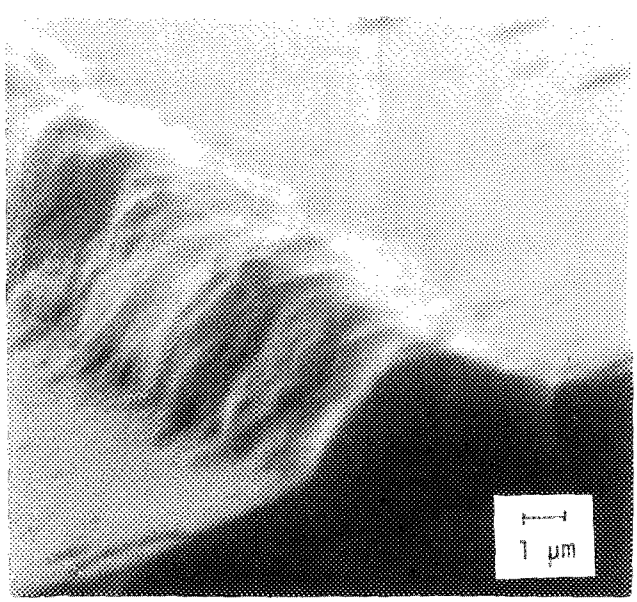


FIG. 3. Scanning electron micrograph of a laser deposited line.

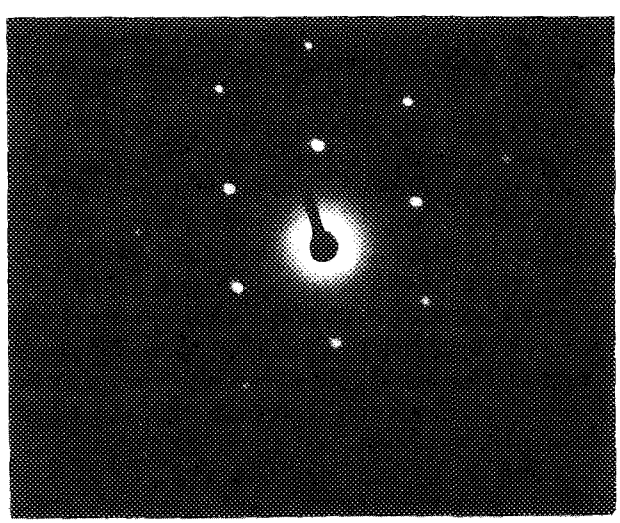

FIG. 4. Transmission electron diffraction pattern of the laser deposited GaP. The zone axis is [110].

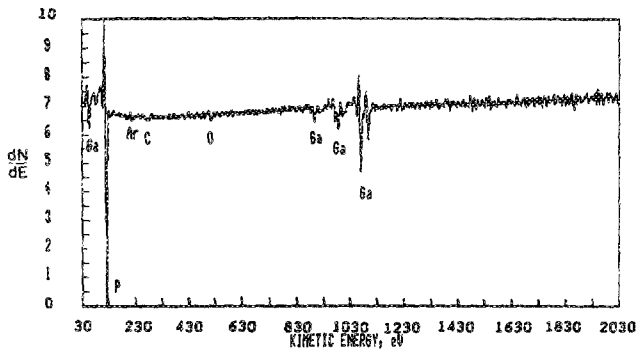


FIG. 5. Auger spectrum of the laser deposited GaP.

example, at TMG partial pressure of 3 Torr, V/III ratio 15, and scan speed 100 $\mu$m/s, the growth/scan first increased with laser power, then stayed approximately even between 0.9 and 1.2 W, and then started to drop again. At higher laser powers the cross-sectional profile has a dip in the middle. Substrate temperatures during the laser scan have been estimated.[10] However, the calculated values are not consistent with our experimental results. Therefore, we are in the process of modifying this theory.

All the results reported above were obtained on (100) GaP orientation. Besides (100), (111) orientation was also examined. For the first few scans ($<10$), the growth/scan of the two orientations is about the same. However, as the thickness of the deposit increased with the number of scans, the growth rate on (100) was higher than that on (111) orientation. For example, under the conditions of Fig. 3 and a scan speed of 100 $\mu$m/s, a corresponding thickness on (111) orientation was 2.4 $\mu$m after 60 scans.

In summary, laser-induced growth of epitaxial GaP structures has been demonstrated using a new phosphorus precursor. Multiple laser scans are required to grow thick epitaxial deposits, where growth/scan gradually slows down. Work is in progress to determine several other aspects of this process such as heteroepitaxy.

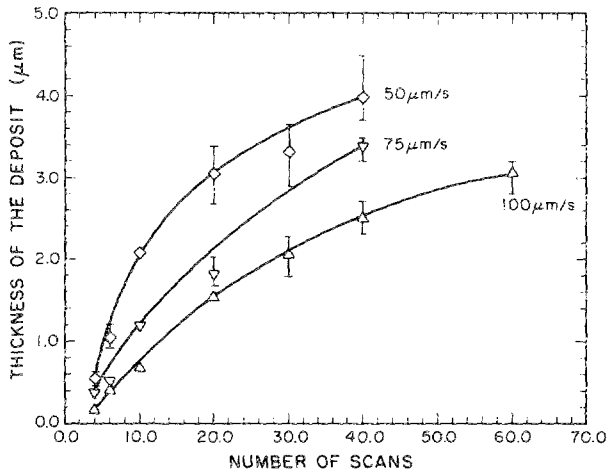


FIG. 6. Dependence of the epitaxial growth on the laser scan speed.

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