Patterned Etching of Infrared Detector Arrays

We have attempted to develop a patterned etching technique for infrared detector arrays based on photo-induced processes. The technique is based on the efficacy of methyl radical etching of II-VI compounds such as HgCdTe and CdTe. Methyl radicals were produced in a pattern above a HgCdTe substrate by photodissociating a radical precursor such as acetone or nitromethane using an excimer laser operating at 193 nm. Neither optical nor scanning electron microscopy could confirm the presence of any etching action. The failure of the proposed technique is ascribed to surface scavenging and/or reaction quenching mechanisms.
PATTERNED ETCHING OF INFRARED DETECTOR ARRAYS

Dist. A. per telecon Dr. J. Dinan
CNVEO ATIN: AMSEL-RD-NV-IRT

6/4/91 CG

Final Report
Prepared under Contract No. DAAB07-90-C-F422

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March 1991
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1. INTRODUCTION

We have tried to develop a laser-based etching technique for infrared detector arrays that is compatible with the ultra-clean, ultra-high vacuum environment of a molecular beam epitaxy apparatus. The etching is to be performed in an add-on chamber which could be evacuated with a turbomolecular or cryopump such that base pressures of $10^{-10}$ Torr could be maintained. A potential major advantage of the laser based technique is that array patterning could be accomplished by optical projection of the laser beam, obviating the need for a physical mask.\textsuperscript{1-4} Thus problems with aligning the mask and minimizing contamination caused by it would be eliminated. We note that the etching step is just the second of four steps in constructing a HgCdTe detector array including wafer growth, etching, metallization to form ohmic contacts, and passivation. The proposed etching technique is not only compatible with the other three steps but may also provide a partial solution to the metallization and passivation steps as well.

The proposed technique is based on the pioneering work\textsuperscript{5} of J.E. Spencer (Plasma Quest) and J.H. Dinan, P.R. Boyd, and H. Wilson (Center for Night Vision and Electro-Optics) who were able to show that HgCdTe was effectively etched by gas phase methyl (CH$_3$) radicals at rates up to 400 Å/min at low temperatures (330 K). The approach used there was to generate CH$_3$ radicals using a secondary afterglow reaction in which fluorine atoms react with methane to form the methyl radicals. Analysis of etched wafers showed that their composition was identical to that of the starting surfaces. A drawback to this approach is that array design must be accomplished using a physical mask (some metal that is not reactive with methyl radicals).
We have generated the methyl radicals photochemically using an ArF-based excimer laser operating at 193 nm and using acetone (and nitromethane) as the precursor molecule. (Photolysis of stable gas phase compounds to produce reactive free radicals has an extensive history and has recently been reviewed by Steinfeld as related to the study of electronic materials.) The chemical etching of the HgCdTe substrate was to be limited by projecting an etch pattern with the laser and flowing an acetone/argon gas mixture over the substrate at sufficient speed and concentration such that the etching action is localized. While this approach is not suitable for very fine features (1 micron) due to gas phase diffusion of the reactive species, it is quite suitable for the comparatively coarse features (50-100 micron etch features) required for detector array fabrication. A schematic diagram is shown in Figure 1.

As mentioned above, the above approach may also offer solutions to the problem of putting ohmic contacts on top of the mesa features. Excimer lasers have been used to produce metal films with metal carbonyl compounds as precursor compounds. If the complementary image (of the original etch image) were projected onto the substrate, metal could be deposited on the mesa features with minimal contamination of the etch features.

The overall objective of the Phase I proposal was to show the efficiency of photo-induced etching of HgCdTe using an ArF excimer laser and acetone as the chemical reagent precursor molecule. The project comprised the following tasks:

- Assembling a simple etching system, including excimer laser, vacuum cell and associated pumping, sample holder, and associated chemical handling system,
- Etching HgCdTe samples using acetone and 193 nm light from the excimer laser,
- Performing optical and scanning electron microscopy on the etched sample to ascertain etching action,
Attempting to etch 100 micron features using photoprojection techniques with subsequent analysis by scanning electron microscopy and Auger spectroscopy.

Unfortunately, no extensive etching could be observed indicating that, at least using acetone and/or nitromethane, this technique was ineffectual.
193nm LASER LIGHT

Mask

(CH₃)₂CO

CH₃MCH₃

HgCdTe

M = Hg, Cd, Te

Photo-Assisted Patterned Etching

Figure 1. Schematic Diagram of Proposed Etching Process
2. TECHNICAL BACKGROUND

Methyl radicals have been shown to etch HgCdTe substrates, presumably by the following overall heterogeneous reaction:

\[
\text{CH}_3(g) + \text{HgCdTe}(s) \rightarrow \text{(CH}_3)_2\text{Cd}(g) + \text{(CH}_3)_2\text{Hg}(g) + \text{(CH}_3)_2\text{Te}(g).
\]

The products are all volatile gases which are used in some HgCdTe deposition techniques (e.g., laser surface chemical epitaxy). Thus the etching reaction is quite "clean" and presumably no substantial carbon incorporation into the substrate occurs. This is in contrast to the use of halogens to etch II-VI compounds, where the cadmium halide salts are comparatively nonvolatile and a cadmium rich reaction layer would remain behind. Thus, controlled production of methyl radicals at or above the surface could be used to etch patterns into II-VI substrates to form detector arrays.

The interaction of lasers (either cw or pulsed) with CH₃-producing precursor compounds offers the hope of such a process. Since the light beam, which is responsible for methyl radical production, can be "patterned" external to the vacuum chamber, no physical mask need be present on the substrate to prevent etching in unwanted areas. The only requirement is that the region of reactive radicals be confined to the small area in which they are initially formed - that is, the diffusion rate and radical recombination rate be balanced such that etching takes place at a reasonable pace in the designated area. This can be arranged by varying the total pressure of the chamber, the partial pressure of the precursor compound, and the laser intensity.
The molecule of choice is acetone, whose photochemistry has been extensively studied in the ultraviolet spectral region. Acetone photodissociates at 193 nm:\(^8-11\)

\[
\text{CH}_3 - \text{C} - \text{CH}_3 \xrightarrow{\text{hv}} 2 \text{CH}_3 + \text{CO}
\]

to produce two methyl radicals and an innocuous carbon monoxide molecule. The cross section for this photodissociation step is \(2 \times 10^{-18} \text{ cm}^2\) at 193 nm\(^{11}\) which means that a 10 mJ/cm\(^2\) laser pulse (quite modest by excimer laser standards) will photodissociate 2% of all the acetone molecules in its path (assuming low acetone concentrations). Thus large quantities of methyl radicals can be generated using low concentrations of acetone.

The key experimental parameters in these experiments include laser intensity, acetone concentration, and total cell pressure. All three quantities must be carefully defined in order to optimize the etching procedure. As shown below, one does not simply want to maximize methyl radical production by increasing laser power and/or acetone concentration. To do so would produce unwanted side effects.

The optimum laser intensity is determined by balancing methyl radical production against the temperature rise induced in the HgCdTe substrate. HgCdTe substrates do not vaporize congruently - the more volatile Hg vaporizes at much lower temperatures than Cd or Te. The maximum temperature rise that would be tolerated is on the order to 80-100 K. While calculations of substrate temperature rise due to laser pulse exposure are inexact, we can estimate that 10-50 mJ cm\(^{-1}\) incident fluence is sufficient to induce such a temperature rise. One other constraint on laser power is the need to limit multiphoton absorption which would lead to formation of ions and non-methyl fragments. The multiphoton absorption cross section for acetone has not been
measured, but we can limit this effect by insuring that the single-photon absorption efficiency, $f$, does not exceed 0.05.

$$f = I_o \sigma \leq 0.05$$

where $I_o$ is the beam intensity in photons cm$^{-2}$ and $\sigma$ the acetone 193 nm absorption cross section. Using the known value of $\sigma(2 \times 10^{-18}$ cm$^2$), we calculate that $I_o$ should be less than $2.5 \times 10^{16}$ photons cm$^{-2}$ or 25 mJ cm$^{-2}$. Thus both substrate temperature and multiphoton absorption effects constrain laser fluence to values on the order of 10-20 mJ cm$^{-2}$. We note that laser ablation of HgCdTe has been shown to occur at approximately 120 mJ cm$^{-2}$ and that the melt threshold of CdTe is 75 mJ cm$^{-2}$.

The maximum acetone concentration is limited by the fact that too high a concentration will attenuate the laser beam before it reaches the substrate surface. The attenuation should probably not be greater than 50%.

$$\frac{I}{I_o} = \exp(-n\sigma) \leq 0.50$$

where $n$ is the acetone concentration, $\ell$ is the pathlength, and $\sigma$ the absorption cross section. Given that $\ell$ is $-5$ cm, the optimum acetone partial pressure should be on the order of 2 Torr.

As stated before, a reasonably anisotropic etch feature can be generated if diffusion is slow compared to the removal rate of methyl radicals by reaction with the substrate or gas phase recombination. This criterion is set by the ratio of the characteristic diffusion time, $\tau_D$, and methyl radical lifetime, $\tau_R$. 

2-3
The characteristic diffusion time, $\tau_D$, is just

$$\tau_D = \frac{L^2}{D}$$

where $L$ is the desired etch feature width and $D_{AB}$ is the diffusion coefficient of species $A$ (CH$_3$) in diluent gas B(Ar):$^{14}$

$$D_{AB} = \frac{1}{\pi \sigma_{AB}^2 [M]} \left( \frac{2 kT}{\pi \mu_{AB}} \right)^{1/2}$$

($[M]$ is the total gas concentration, $\sigma_{AB}$ the collision diameter of $A$ with $B$, and $\mu_{AB}$ is the reduced mass of $A$ and $B$).

The characteristic methyl radical lifetime is conservatively estimated by:

$$\tau_R = (\tau_{R[CH_3]})^{-1}$$

where $k_R$ is the recombination rate constant in the high pressure limit ($4 \times 10^{-11}$ cm$^3$ s$^{-1}$).$^{15}$ Thus the quantity, $\tau_D/\tau_R$ reduces to:
where \( C \) is a constant

\[
C = L^2 k_R \pi \sigma_{AB}^2 \left( \frac{2kT}{\pi \nu_{AB}} \right)^{-1/2}
\]

related to molecular parameters, cell temperature, and the desired etching features. Assuming \( T = 295 \text{ K} \), \( \sigma_{AB} = 3.6 \text{Å} \), and \( L = 10 \text{ cm}^{-2} \), this reduces to:

\[
\frac{\tau_D}{\tau_R} = 0.46 \ P_{\text{total}} \times P_{\text{CH}_3}
\]

where \( P_{\text{total}} \) and \( P_{\text{CH}_3} \) refer to the total cell pressure and partial pressure of methyl radicals respectively in units of Torr.

In a preceding set of calculations, we determined that a 25 mJ cm\(^{-2}\) 193 nm laser pulse would photodissociate 5% of an optimum acetone partial pressure of 2 Torr, producing a partial pressure of 0.2 Torr of \( \text{CH}_3 \). If we want \( \tau_D/\tau_R > 10 \), then

\[
P_{\text{total}} = \frac{\tau_D}{\tau_R} (0.46 \ P_{\text{CH}_3})^{-1} = 100 \text{ Torr}
\]

Given that the range of experimental conditions has been established, we can now calculate the expected etching rate. The simplest approximation is to
set the etching rate equal to the product of the initial flux of methyl radicals to the surface and a characteristic etching period after the laser pulse:

\[ R = J \times \Delta T \]

where the flux, \( J \), is:

\[ J = \frac{[\text{CH}_3]_0 g}{4} \]

([CH\(_3\)] is the initial methyl radical concentration and \( g \) is the molecular velocity of the radical) and \( \Delta T \) is just the radical recombination time, \( \tau_R \):

\[ \Delta T = \tau_R = \left( k_R [\text{CH}_3] \right)^{-1} \]

Combining these two expressions, we see that the etching rate is a constant,

\[ R = \frac{g}{4 k_R} \approx \frac{6 \times 10^4}{(4 \times 10^{-11})} = 4 \times 10^{14} \text{ cm}^{-2} \text{ pulse}^{-1} \]

on the order of a monolayer per pulse. At a laser repetition rate of 100 Hz, this would produce an etching rate of 100 \( \mu \text{m hr}^{-1} \). The rest of this report describes efforts to etch HgCdTe based on the results of this feasibility study.
3. EXPERIMENTAL

The vacuum apparatus used in these experiments was a 4" o.d. six-way cross with conflat flanges. The cell was lined with a cylindrical form of sheet metal effectively providing an internal flow cell with ports at both ends for gas introduction and pumpout. Small apertures allowed for optical and mechanical access (for the laser beam and sample mount) as well as a pressure monitoring port. Figure 2 provides a schematic of the cell.

The HgCdTe sample is a 20 μm thick epitaxial layer of Hg₀.₈Cd₀.₂Te grown on CdTe substrates using the technique of Closed Space Vapor Phase Epitaxy. The substrate is mounted using gallium solder on an aluminum baseplate which in turn is attached to a UHV feedthrough (Huntington) which allows for external adjustment of the sample height (2.5 cm travel) as well as rotating the sample in and out of the laser beam. The samples, provided by the Night Vision Laboratory, were soaked in several warm acetone baths to remove the covering layer of photoresist, etched in a 1% solution of bromine in methanol for two minutes to remove the native oxide layer, and rinsed in several baths of isopropyl and methyl alcohol, before mounting. All chemicals were of reagent or HPLC grade.

The gas handling system is shown in Figure 3. Argon gas at a set pressure (typically 1000 Torr) is flowed (bubbled) through a glass bulb filled with acetone which is maintained at either ice temperature (273 K) or room temperature (295 K). The pressure in the bulb is monitored using a (Baratron) capacitance manometer. The volume flow is controlled by a leak valve (Whitey) before entry into the vacuum cell. The pressure in the vacuum cell is controlled separately by a gate valve (Huntington) at the cell exit and measured using another capacitance manometer. All gas flows are measured using an electronic flow monitor (Sierra). The gas flow, once past the cell gate valve, passes through a liquid nitrogen trap (Norcal) to remove most of the acetone vapor before entering a mechanical pump (Alcatel).
Figure 2. Schematic of Etching Vacuum Cell
Figure 3. Schematic of Chemical Precursor Preparation System
The 193 nm light is provided by an ArF excimer laser (Questek) operating at 10 Hz. The output of this laser was approximately 40 mJ per pulse with a pulse shape of 1 x 2 cm. Given that the energy fluence, 20 mJ cm$^{-2}$, was nearly optimum for these experiments, no focusing or defocusing was used. The laser beam was directed through a 250 μm x 1 cm long horizontal monochromator slit to produce a reasonably narrow etch pattern before entering the vacuum chamber through a conflat-flange mounted MgF$_2$ window (Harshaw). In order to minimize deposition of organic matter on the window and to reduce the effective distance of interaction between laser beam and acetene, a purge flow of pure argon (amounting to ~20% of the total gas flow) was introduced through an injector ring concentric with the window effectively flushing out the cell arm. No window contamination after ten hours of laser irradiation could be seen.

In a typical experiment, the cleaned and etched HgCdTe sample was placed in the vacuum cell after mounting on a aluminum plate. The cell was evaluated and pure argon was flowed through the system for at least 15 minutes in order to flush air and water out of the cell. At that point, the gas flow was switched over to an acetone/argon mixture. The partial pressure of acetone in the cell can be calculated from:

$$P_{acetene} = \frac{P^o(T)}{P_{bulb}} \times P_{cell}$$

where $P^o(T)$ is the acetone vapor pressure above its liquid at a given bath temperature, $P_{bulb}$ is the total pressure in the mixing bulb, and $P_{cell}$ is the total pressure in the cell. Table 1 presents values of $P^o(T)$ for both acetone and nitromethane. The sample was exposed to this flow for another 15 minutes to allow the surface to become equilibrated with the acetone vapor. At this point the sample and laser beam were aligned by rotating the aluminum plate so that is rear surface faced the laser beam pattern. (Slivers of fluorescent
Table 1 - Precursor Vapor Pressure (Torr)\textsuperscript{a}

<table>
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<tr>
<th>T (k)</th>
<th>Acetone</th>
<th>Nitromethane</th>
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<tbody>
<tr>
<td>233\textsuperscript{b}</td>
<td>5.5</td>
<td>0.44</td>
</tr>
<tr>
<td>273</td>
<td>61.4</td>
<td>8.1</td>
</tr>
<tr>
<td>295</td>
<td>175.4</td>
<td>28.8</td>
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</tbody>
</table>

\textsuperscript{b}Low range of typical Freon refrigerator

Glass (Pyrex) which had been aligned with the edge of the HgCdTe sample were epoxied onto the rear of the plate. The sample plate was raised or lowered until the fluorescent glass was irradiated by the 250 μm wide slit of laser light. We estimate that we could align the laser to the bottom of the sample to within 500 μm (twice the slit width). The sample was lowered 2 mm and rotated back into the laser beam for a period of approximately 1 hour where it was exposed to ~36,000 laser pulses. When new parameters were set, the sample was lowered another 2 mm between runs to produce a fresh etching surface.

As noted in Table 2, we also attempted to use an alternative precursor molecule, nitromethane ($\text{CH}_3\text{NO}_2$). The photodissociation of nitromethane has a larger cross section than acetone:

$$193 \text{ nm}$$

$$\text{CH}_3\text{NO}_2 \longrightarrow \text{CH}_3 + \text{NO}_2 \quad \sigma = 7 \times 10^{-18} \text{ cm}^2$$
although producing one methyl radical per molecule. This process also produces a yellow fluorescence which is visible in the cell and confirms that the laser beam does indeed reach the HgCdTe surface.

Table 2 presents a matrix of etching parameters which were attempted. Trials were made at two different total pressures and at 2 separate acetone pressures for each total pressure. Once etched, samples were flushed with acetone/Argon vapor for 15 minutes in situ, removed from the cell, removed from the aluminum mounting plate, and wrapped in lens tissue and plastic sheet and shipped to the Night Vision Laboratory for analysis.

Table 2 - Experimental Operating Parameters

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<th></th>
<th>Acetone</th>
<th>Nitromethane</th>
</tr>
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<tbody>
<tr>
<td><strong>Cell Pressure (Torr)</strong></td>
<td>5 30</td>
<td>5 30</td>
</tr>
<tr>
<td><strong>Precursor Pressure (Torr)</strong></td>
<td>0.25 0.75 2.0 6.0</td>
<td>0.04 0.14 0.24 0.86</td>
</tr>
<tr>
<td><strong>Precursor Temperature</strong></td>
<td>273 295 273 295</td>
<td>273 295 273 295</td>
</tr>
<tr>
<td><strong>Laser Power (mJ cm⁻²)</strong></td>
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<td>20</td>
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<tr>
<td><strong>Laser Pulses</strong></td>
<td>36000</td>
<td>36000</td>
</tr>
<tr>
<td><strong>Gas Flow Rate (sccm)</strong></td>
<td>3500</td>
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</tr>
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Neither optical nor scanning electron microscopy (at magnifications up to 400 and 8000 respectively) provided any evidence for successful etching regardless of precursor, precursor concentration, and/or total cell pressure. This would seem to indicate that methyl radicals do not etch HgCdTe under the conditions used here. This negative result is extremely surprising in light of the work of Spencer and co-workers who were able to etch similar samples with methyl radicals produced by the reaction of methane with fluorine atoms. It should be noted that both experiments involve similar instantaneous concentrations of methyl radicals.

It is clear from these apparently contradictory results that the analysis presented in the technical background is flawed in that it neglects surface quenching processes. Among these processes are recombination of mobile methyl radicals on the surface itself.

\[
\text{CH}_3(s) + \text{CH}_3(s) \rightarrow \text{C}_2\text{H}_6(s)
\]

\[
\text{C}_2\text{H}_6(s) \rightarrow \text{C}_2\text{H}_6(g)
\]

to produce ethane (or some other hydrocarbon such as ethylene), or to scavenging reactions involving adsorbed acetone:


\[
(CH_3)_2 CO(g) + CH_3(s) \longrightarrow CH_3COCH_2(s) + CH_4(s)
\]

\[
CH_3COCH_2(s) + CH_3(s) \longrightarrow CH_3COC_2H_5(g)
\]

\[
(CH_3)_2 CO(g) + 2CH_3(s) \longrightarrow CH_4(g) + CH_3COC_2H_5(g)
\]

leading to the production of methane and methyl ethyl ketone. Another possibility is that precursor adsorption blocks all potential reaction sites and thus prevents methyl radical induced etching.

Unfortunately, little is known qualitatively or quantitatively about these processes. Given the successful etching of HgCdTe by Spencer and co-workers, it would appear that the scavenging or blocking process are the more likely culprits. The only reactive gas other than methyl radicals produced in the Spencer flowing afterglow apparatus is hydrogen fluoride. Although Hg, Cd, and Te can form highly stable fluorides in exothermic reactions with HF,\(^{17}\) no evidence for any metal salts is found (CdF\(_2\) is not volatile at moderate temperatures).\(^{18}\) Thus, it seems that reactive etching by methyl radicals occurs at a much faster rate than either methyl radical recombination or substrate reaction with HF.

Additional insight is provided by work performed at Hughes Research Laboratory,\(^{20}\) in which attempts to etch CdTe using photochemically produced methyl radicals (under conditions almost identical to those used in this experiment) also failed. But they do report that both Te metal and Te-rich CdTe are etched quite effectively in this fashion.\(^{20}\) They note that methyl radicals form much stronger bonds with Te than with Cd\(^ {21}\) and that the initial Cd-CH\(_3\) bond which must be formed in the process of forming Cd(CH\(_3\))\(_2\) is quite
weak (-12 Kcal mole\(^{-1}\)).\(^{22}\) Thus the inability to etch away Cd (and Hg in the case of HgCdTe) is simply due to a kinetic limitation - i.e., the methyl radical scavenging by acetone outpaces the etching process. The similar negative results with nitromethane as the methyl radical precursor is consistent with this picture. Both acetone and nitromethane have oxygen atoms whose high electron densities would facilitate surface adsorption. In addition, both molecules can participate in similar scavenging mechanisms. Thus, a photochemically based methyl radical etching process for HgCdTe requires a much less reactive precursor molecule.

In conclusion, the quest for a laser-based projection patterning and etching process for ternary II-VI compounds remains unfulfilled. We note that Hughes Research Laboratory has shown that CdTe can be laser etched using a 248 nm KrF excimer laser without ablation or non-reversible stoichiometry changes. Unfortunately, HgCdTe is much less stable than CdTe with respect to thermal temperature spikes and may not exhibit similar behavior. Finally, we warn that any simple chemically assisted etching scheme, laser based or not, may cause unwanted complications that will require further process modifications.
5. REFERENCES


5-1
17. P.D. Brewer, private communication.


