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Laser etching and dry processing

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Abstract. Controlled, anisotropic etching of different materials commonly used in microelectronics is an important processing step in microfabrications. During recent years it has been demonstrated that lasers can be used for initiating and enhancing the etching process in many gas–solid (dry processing) and liquid–solid (wet processing) systems. The laser-induced reaction could be either photochemical or thermochemical. Using laser etching technique a variety of materials such as Al, Ta, Ni/Fe, GaAs, InP, Si, SiO_2 mylar, different polymers and superconducting materials have been processed. In this paper we briefly review these laser etching experiments.

Keywords. Laser; etching process.

1. Introduction

One of the several fields where lasers are in regular use is the electronic industry. Their applications in two main technological processes of microelectronics have been well established for over a decade (Metev 1986). These are:

i. Modification of the functional parameters of thin-film devices, such as resistor trimming, functional trimming of hybrid integrated circuits, trimming of quartz resonators and filters, etc.
ii. Mounting of microelectronic components and devices, such as micro-welding of electrical connections, sealing of device frames and scribing of semiconductors, etc.

In the last few years some new and interesting applications of lasers in this field have emerged. The special features of laser radiation such as coherence and wide range of output power, and its spectral and temporal characteristics have made feasible the use of lasers to directly modify, in controllable manner, some properties of materials or even to synthesize new materials. Owing to these characteristics, lasers are now being used not only in the auxiliary technological processes mentioned above but also in the basic ones, such as deposition, implantation, annealing, etching, etc.

One of the special features of laser processing techniques is that they do not need use of the elaborate lithographic technique since the laser beam can be focused on within-micrometre-size regions without affecting neighbouring material or adjacent circuits.

The new technological processes that have received considerable attention in recent years include laser chemical vapour deposition of insulating, semiconducting and metallic materials, laser etching of microelectronic parts using gaseous and liquid etchants, mask and circuit pattern repair using photo-resist and lift-off techniques, and laser annealing. In this paper we will briefly discuss laser etching and dry processing of various materials. For more details, the reader is referred to recent review papers on this topic (Ehrlich *et al* 1980; Houle 1984; von Gutfeld 1984; Yardley 1985; Lehmann 1986; Metev 1986).

2. Dry etching process

The aim of the etching process is to convert the solid into a chemical form that can then be easily removed from the reaction zone.

In the production of integrated circuits (IC) and very large scale integrated (VLSI) circuits in microelectronics, a pattern is required to be transferred from the mask onto the substrate. Pattern transfer from the mask onto the substrate can in principle be done by an additive process like "lift-off" or a subtractive process like etching. However, since lift-off processes are rather difficult to be reproducibly executed in a manufacturing environment, most pattern transfer processes are performed today by etching process.

In conventional wet chemical etching process the solid surface is etched by dipping it into some chemicals, acidic or basic solutions. This technique, which has long been the standard method of pattern delineation in Si technology (Kern and Deckert 1978), has the big advantage of being very selective and fast, but it usually leads to an isotropic etch profile (figure 1) because the etch front moves at the same rate in the vertical as well as in the horizontal direction. Anisotropic liquid etching only occurs in crystalline materials when etch rates along different crystallographic orientations can vary by a large extent.

Over the past ten years a steady transition from traditional wet etching to anisotropic dry etching has taken place. In dry etching solid surface is etched in a gaseous environment. There are certain advantages of the dry etching process. The etching is anisotropic in crystalline as well as in polycrystalline or amorphous materials. The adherence of the masking film to the substrate is not critical. In wet processing the mask could become loose very quickly upon immersion into acidic solutions. Huge amounts of toxic liquids have to be disposed off. In dry process exhaust gases can be passed through a scrubber and the amount of toxic waste is relatively small.

Dry etching is usually initiated by a discharge plasma (Lehmann 1986). The plasma-assisted dry etching techniques can be broadly classified into glow discharge method and ion-beam method. In the glow discharge method the plasma is

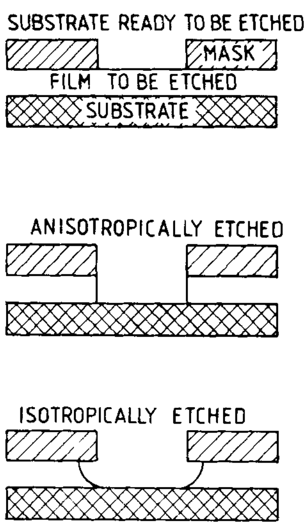

Figure 1. Isotropic and anisotropic etching of a masked thin film substrate.

generated in the vacuum chamber where the substrate to be etched is placed. In the ion-beam method the plasma is generated in a separate chamber from which ions are extracted and directed towards the substrate by a number of grids.

Figure 2 shows, schematically, a dry etching system. The r.f. field produces the glow discharge. The etching gas gets excited, ionized or dissociated via electron collisions and produces reactive ions and radicals which react with the substrate and cause etching. After the reaction has taken place, the reaction product has to be desorbed from the surface. Higher the vapour pressure of the product, faster will it be desorbed. Etching gases such as O_2, CF_4, BCl_3 and CCl_4 have been used and etching of Si, Al and polymers has been achieved.

In O_2 discharge O_{2^+} ions are formed and this has been used to etch polymers such as photoresist HPR 204. Anisotropic etching of Al films, which is one of the most difficult processing jobs in VLSI manufacture was obtained in BCl_3 plasma (Lehmann and Widmer 1983).

For more details about the mechanisms of dry etching process the reader is referred to Lehmann (1986) and the references therein.

3. Laser etching process

Experiments have been recently carried out to evaluate laser-activated photochemical and thermochemical etching (Baklanov *et al* 1974; Chuang 1980; Ehrlich *et al* 1980; von Gutfeld and Hodgson 1982). Laser etching has been demonstrated in both gas–solid and liquid–solid systems with pulsed as well as CW lasers of wavelength ranging from 10·6 microns to 193 nm. The laser beam is focused near or on the surface of the substrate kept in gaseous or liquid etchant for etching. This initiates or enhances the etching reaction locally. Laser photo-etching involves a combination of physico-chemical processes that lead to controllable material removal from the surface of a solid.

The basic interaction processes between the laser and the etchant or the substrate to be etched can be broadly classified as follows:

i. The etchant directly absorbs the laser radiation by single or multi-photon absorption process and produces reactive atoms, ions or radicals through dissociation, ionization or excitation. These in turn react with the substrate, forming

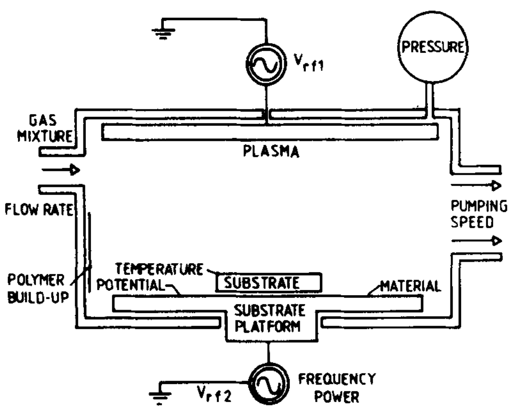

Figure 2. Schematic diagram of a parallel plate dry etching system.

easily removable solid salt or volatile compound. This is a photochemical process and is dependent on laser wavelength.
ii. The surface of the substrate gets locally heated by the focused laser beam and the local heating either enhances the etching reaction or initiates thermal excitation or dissociation of the etchant to produce reactive species which in turn cause etching of the substrate. This is a thermochemical process.
iii. The laser radiation could get absorbed in semiconductor materials and produce electron–hole pairs which enhance the etching process.
iv. The substrate decomposes under the laser action into volatile compounds.
v. The substrate is ablated directly by the intense laser pulse.

In the last two processes no etching agent is required.

3.1 *Laser etching in gaseous environment*

Photochemical and thermochemical gaseous dissociations to produce etching have been investigated with CO_2, Ar-ion, frequency-doubled Ar-ion and excimer lasers.

Table 1 gives some examples of laser etching experiments (Yardley 1985). Simple gases such as Br_2, Cl_2 and HCl, alkyl halides such as CH_3Br, CH_3I and CH_3Cl, as well as SF_6 and XeCl have commonly been used for etching since halogen radicals are easily produced and react readily with many materials to form volatile species. In order to illustrate the etching process some of the experiments are discussed here.

Ehrlich *et al* (1980) have obtained photoetching of both n-type InP and GaAs using CH_3Br, CF_3I and CH_3Cl in conjunction with a 4 mW, 257·2 nm uv laser. The mechanism of CH_3Br etching of GaAs is described by the reactions

Table 1. Laser etching experiments (Yardley 1985).

Material	Etchant	Laser
Semiconductors		
Si	Cl_2, Br_2, XeF_2	Ar-ion
Si	XeF_2, SF_6	CO_2
Ge	Br_2	Ar-ion
GaAs	Br_2, Cl_2	Ar-ion
GaAs, InP	CF_3Br etc.	Excimer, Ar-ion
GaAs, CdS	$H_2SO_4+H_2O_2$, HNO_3	Ar-ion
Conductors		
Al	HNO_3, H_3PO_4	Ar-ion
Ta	SF_6, XeF_2	CO_2
Ni/Fe	SF_4, CF_4, etc.	Ar-ion
Insulators		
SiO_2	Cl_2	Ar-ion
SiO_2	CF_3Br, HF	CO_2
Mylar	O_2, air	Ar-ion
Al_2O_3/TiC	CCl_4, SF_6	Ar-ion, Nd: YAG
Mn/Zn ferrite	CCl_4, SF_6, etc	Ar-ion
PET, other polymers	—	Excimer
PMMA	—	Excimer
Nitrocellulose	—	Excimer

$$CH_3Br \longrightarrow CH_3 + Br$$

$$Br + GaAs \longrightarrow \left| \begin{matrix} GaBr \\ AsBr \end{matrix} \right| \begin{matrix} gas \\ ads \end{matrix} \uparrow .$$

The Br is adsorbed on the GaAs surface. This is followed by the formation of volatile adsorbates. The etching rate was about 9·7 Å/s for 100 W/cm^2 power density and 750 torr of CH_3Br. The rate increased almost linearly with laser intensity over a wide range. The etching was localized to the area of laser irradiation and resolution as high as 1·5 microns was obtained.

On laser irradiation of the substrate, the rise of temperature also activates or enhances the etching process in the presence of weakly bound halogen atoms. One example of such a thermochemical etching process is the etching of Si in XeF_2 atmosphere with the CO_2 laser. In this process it is believed that the laser promotes an increase in the striking rate of XeF_2 on the Si surface, which leads to an increase in the net surface reaction rate. The laser radiation also produces surface excitation and a rearrangement of the atoms to enhance the formation of the volatile adsorbate SiF_4. The effects are independent of laser frequency over the range 920–980 cm^{-1} and are thus not due to direct photolysis of the XeF_2 gas.

Lasers have also been used to enhance the plasma etching process. Reksten *et al* (1986) have obtained laser enhancement of Si etching by up to 1·8 times compared to dark etch rate in CF_4/O_2 and NF_3 plasma etchants. The etch rate increased with increase of laser power and laser frequency and also was found to be dependent on the dopant concentration in Si. At a laser power density of 1 kW/cm^2, for instance, the etch rate enhancement obtained with 350 nm light was ~3·5 times greater than that obtained with 514 nm light and ~5·5 times greater than the effect at 647 nm. The etching rate decreased with increase of doping. While the etch rate enhancement at high laser power densities was attributed to thermal effects, at low power densities it has been attributed to increase in the number of photogenerated carriers that reach the surface. Since plasma etching is preferentially more where the laser is focused, such laser-enhanced etching has potential application as a technique for maskless processing for plasma etching.

Recently Treyz *et al* (1987) have demonstrated etching of deep trenches in crystalline silicon with Ar-ion laser in Cl_2 ambient. The shape of the etched trench was greatly influenced by laser beam polarization. Maximum depth of about 12 microns at 8 W laser power and scan speed of 500 microns/sec was reported in 200 torr Cl_2 ambient. These results have been qualitatively explained on the basis of a thermal process through which a molten silicon surface is formed on laser irradiation resulting in enhanced etch rates.

3.2 *Laser etching in solution*

Laser etching of certain conductors, semiconductors and ceramics for micromachining purposes has been achieved using liquid etchants, including H_2SO_4 and H_2O_2 mixtures, as well as solutions of HCl, HNO_3, H_3PO_4 and KOH (Osgood *et al* 1982; Bjorkholm and Ballman 1983). Materials that were successfully etched include Al, semi-insulating GaAs, n-type GaAs, CdS, InP, Si and ceramic materials such as alumina/TiC, Mn/Zn ferrite and alumina. On compound semiconductors blind via holes, through holes (in ~125-micron-thick sample) and gratings were etched with any one of several visible and near-UV wavelength lasers. Using a holographic set-up an optical quality grating with better than 0·5 micron resolution was obtained. In semiconductors the mechanism of etching at low power densities is described in terms of electron–hole pair production through absorption of the laser energy. For example, the etching of GaAs in the oxidative solution $H_2SO_4/H_2O_2/H_2O$ under the action of Ar-ion laser radiation of photon energy more than the band gap energy is postulated to be due to slow Ga ion transition into the solution and to the oxidation of As ion to an easily removable oxide:

$$GaAs + 6\,h \longrightarrow Ga^{+3} + As^{+3}.$$

The etch rate was measured for 488 nm, 514·5 nm and 632·8 nm laser wavelengths and it was found to increase by 1·5 times when the laser wavelength was changed from 632·8 nm to 488 nm. At 1·15 micron wavelength, which oorresponds to photon energy less than GaAs band gap, no significant etching was observed. Etch rates are dependent on the pH of the solution, crystal orientation and doping level. Etch rates of up to 2 microns/min for 100 W/cm^2 of laser power density were obtained (von Gutfeld 1984).

Podlesnik *et al* (1986) have obtained vertical, higher-aspect features in GaAs samples of different crystal orientations through the rapid ultraviolet-induced etching in diluted HNO_3 aqueous solution. High-aspect features are an important requirement in the fabrication of advanced electronic and microelectronic devices.

The etching of ceramic materials, Si in different orientations, and several optically absorbing glasses was achieved in liquids when irradiated by a laser beam at a very high intensity, of the order of 10^6–10^7 W/cm^2. At these laser power densities localized melting and etching occurred simultaneously. For the etching process it was postulated that melting and/or vaporization contributed to (i) direct removal of material, (ii) increasing the surface area in contact with the etchant, and (iii) local temperature increase of both sample and etchant to promote thermally activated kinetics.

There are many solution-phase etching processes that exhibit a steep dependence of temperature on reaction rate. In such cases laser excitation can cause large enhancement in the etch rates. For example, the laser irradiation of aluminium by Ar-ion laser enhanced the etch rate in aqueous solution by a factor of 10^6 (Tsao and Ehrlich 1983).

3.3 *Etching by direct laser photochemical process*

A different kind of photochemical etching process, unique to laser excitation, was reported by Srinivasan and coworkers (Srinivasan and Leigh 1982; Srinivasan and Mayne-Banton 1982; Srinivasan *et al* 1986). In this process organic polymers could be cleanly ablated by pulsed excimer laser excitation. For typical organic polymer material, particularly material containing aromatic rings, the absorption cross-section is very high at short wavelengths. For example, in polyethylene terephthalate (PET) the absorption depth at 193 nm is approximately 0·1 micron. Furthermore, the energy per photon is more than sufficient to break simple molecular C–C or C–H bonds. Thus when the PET is irradiated with laser radiation of short wavelengths the molecules dissociate by photon absorption. The material ablates out, primarily because of the large difference between the specific volumes of the solid polymer and the gaseous molecules which are the decomposition products. Srinivasan and coworkers (Srinivasan *et al* 1986) have found that, in addition to the photochemical effect described above, a thermal effect was also responsible for the etching process. This technique has been tried with different types of polymers such as polyimide, polymethyl-methacrylate (PMMA), nitrocellulose, TNS2 (an IBM proprietary material), photoresist, etc.

3.4 *Laser etching by direct ablation*

Recently Inam and coworkers (Inam *et al* 1987) have demonstrated that Y-Ba-Cu-O superconducting thin films can be etched efficiently using a pulsed excimer laser (248 nm, 30 ns). Material can be removed in uniform layer-by-layer manner without any change in the chemical composition of the remaining film. Etch depth increased linearly with number of laser pulses over a wide range of incident laser energy densities. An etch threshold energy density of 0·11 J/cm^3 was observed and etch rate per pulse scaled linearly with the logarithm of the incident energy density. The temperature of the region irradiated by laser pulse rises to much beyond the melting point of the substrate and material from that zone ablates out leaving behind a clean etched surface. These experimental observations are explained satisfactorily by a linear absorption model.

4. Conclusions

Based on recent and continuing research it appears evident that lasers will continue to play an increasingly important role in the field of microelectronics. Laser etching of various materials commonly used in this field has been demonstrated. Its acceptance as a routine process in the manufacture of microelectronic parts appears to be at hand in the not-too-distant future.

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