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Fabrication of micrometer-scale structures on GaAs and GaAs/AlGaAs quantum well material using microcontact printing

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Abstract. Microcontact printing (μCP) was used in conjunction with self-assembled monolayers (SAMs) of hexadecanethiolates to fabricate gold etch masks on GaAs and GaAs/AlGaAs quantum-well substrates; patterns in the mask were transferred into the semiconductor with an anisotropic dry chemical-etch process. The measured luminescence efficiency of the etched features in GaAs/AlGaAs was similar to that of samples patterned using conventional lithography; this observation indicates that no mechanical or chemical damage is incurred in the μCP process.

Recently, several new fabrication techniques have been devised to form submicrometer features in semiconductor crystals for use in micromechanical, microchemical, or micro-optical sensors. In some cases, the requirements for relatively modest resolution ($\sim$ 1–20 μm), combined with geometry of the sensor surfaces, make the use of a non-lithographic approach to patterning attractive. For many of these applications it is important to form structures in GaAs, for example, the use of GaAs can in principle allow the incorporation of a monolithic optical source or modulator. Unfortunately, this III–V material is less robust than silicon and process-induced mechanical or electrical damage incurred during patterning must be carefully understood and controlled.

This paper describes a new non-lithographic technique —microcontact printing—for fabricating an etch mask of gold supported on GaAs, and the subsequent use of dry anisotropic chemical etching to transfer this pattern into single-crystal GaAs and thin epitaxially-grown InGaAs/AlGaAs multi-quantum-well materials (MQWs). In the case of the MQW samples, the etched material is examined by *ex situ* photoluminescence. This experiment serves as a sensitive test of any mechanical or chemical damage resulting from the contact-printing process, since any significant damage in the etched structures would be detected by loss of luminosity by the quantum wells.

Microcontact printing [1–3] (μCP) of self-assembled monolayers (SAMs) of alkanethiolates on gold has been used to pattern nanometer-thick resists, with edge resolution of less than 50 nm in the best cases [2]. An elastomeric stamp used in μCP is fabricated by casting poly(dimethylsiloxane) (PDMS) on a master (usually a patterned photoresist that is fabricated photolithographically, although non-lithographic techniques can also be used) which contains the relief structures to be reproduced. The stamp can also be fabricated by casting PDMS on a silicon master that has been etched anisotropically using a patterned etch mask [4]. After 'inking' the stamp with an alkanethiol, a patterned SAM film is formed by conformal contact between the stamp and a gold film; the conformality in the process relaxes the requirement for substrate surface flatness. The SAM pattern can then be used as an etch mask to transfer the pattern into an underlying substrate or film [5]. In the dry, chemical etching technique—UV cryoetching [6, 7]— used here, a layer of molecular chlorine is physisorbed (at approximately 140 K) on the surface of GaAs and GaAs/AlGaAs; irradiation of this adlayer with a pulsed UV laser generates surface-localized atomic chlorine that gives rise to anisotropic etching. Etching is initiated by direct photoabsorption by the adsorbed chlorine molecules via an intermolecular charge-transfer band present only in the condensed phase [8]. Since it does not rely on the bombardment of a massive particle for etching, the surface is not damaged [9]. Because the sample is held at low temperature, spontaneous thermal etching of the sample is suppressed, and the etching reaction proceeds only where illuminated; the resolution is limited, for shallow etching, only by the aerial optical image at the surface. Cryoetching has recently been used in the fabrication of damage-free quantum features of 90 nm radius [9], using a surface mask formed by conventional e-beam lithography. Since

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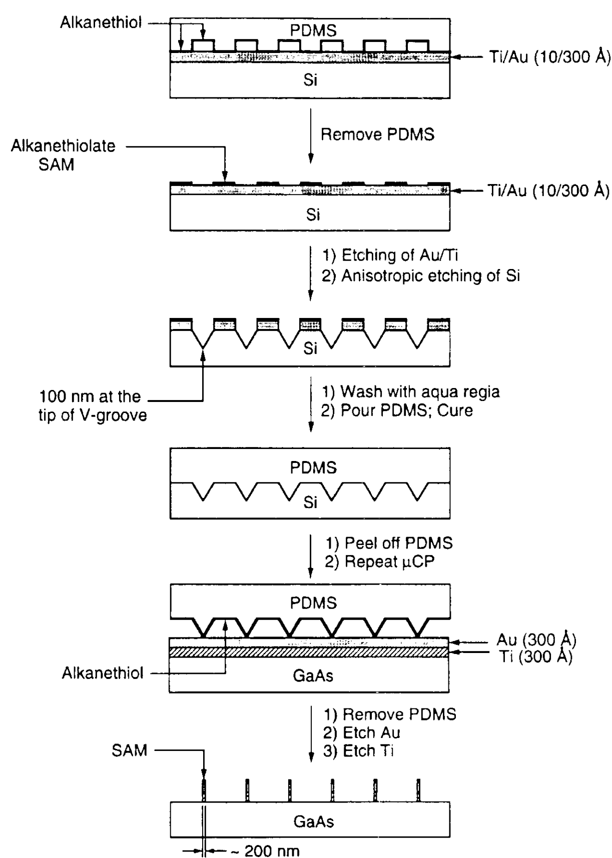

Figure 1. Schematic of microcontact printing and wet-chemical etching procedures to fabricate an elastomeric stamp and then form an etch mask on gallium arsenide.

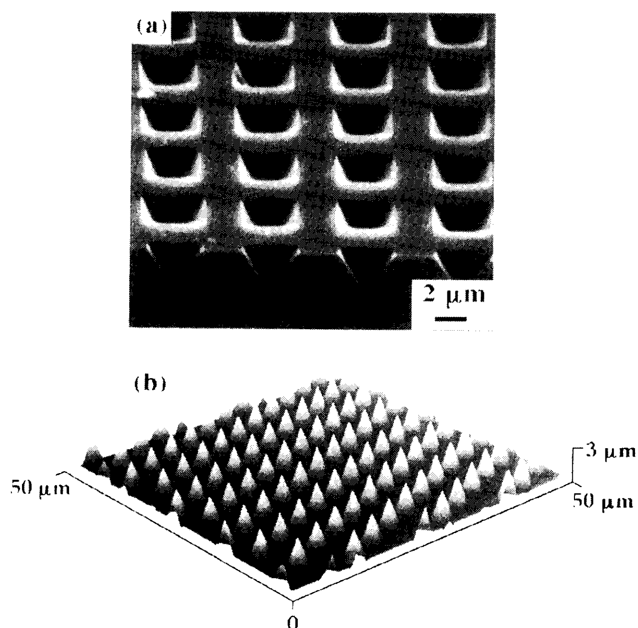

Figure 2. (a) Electron micrograph of a silicon master that has been patterned by anisotropic etching. The shape of the pits are inverted pyramids with sharp tips at the bottom (< 100 nm). (b) Scanning probe micrograph of the elastomeric replica of this etched silicon master.

the etch process is the result of a purely 'chemical' removal process, it provides a test process for probing the chemical and structural quality of a semiconductor surface after the fabrication of the surface mask using μCP.

For the experiments described here, a SAM of hexadecanethiolate patterned by μCP was used to fabricate a mask for dry-etch pattern transfer. The stamp used here for μCP was made by a combination of μCP and anisotropic wet etching of a silicon substrate to achieve fine feature width. The efficacy of μCP, in conjunction with cryoetching, to form submicrometer structures was investigated by etching (100) n-GaAs ($\sim 10^{17}$ cm^{-3}) substrates. In addition, the suitability of this combination of processes to fabricate structures containing quantum wells was tested by etching MOCVD (unintentionally doped) GaAs/AlGaAs MWQ material; diagnostic measurements of any etch damage were made using the photoluminescence efficiency of the resulting structures.

Figure 1 illustrates procedures involved in fabricating a silicon master for making an elastomeric stamp and an etch mask for GaAs. A SAM of hexadecanethiolate was patterned with existing μCP stamps (50% contact area) on a gold film (300 Å of Au with 10 Å of Ti as an adhesion promoter) supported on a silicon wafer (with (100) orientation). The pattern of the SAM layer was transferred to the underlying gold by submersion of the sample in an aqueous solution of $Fe(CN)_6^{3-}/Fe(CN)_6^{2-}/S_2O_3^{2-}$ (0.1 M/0.01 M/0.1 M in 1 M KOH) [10], note also that a solution of CN^-/O_2 can be used [11]. Etching occurred only on the regions of gold unprotected by the SAM film, and the exposed gold was etched completely up to the silicon surface. Anisotropic etching of silicon was performed using KOH/2-propanol [12, 13] so as to produce etch features that were 'inverted pyramids' with dimensions of approximately 100 nm^2 measured at the bottom of each pit. The gold mask was removed in *aqua regia* ($HCl:HNO_3$ = 1:1 (v:v)); the silicon wafer was treated in a solution of peroxysulfuric acid ($H_2O_2:H_2SO_4$ = 1:3 (v:v)) and silanized using the vapor of octadecyltrichlorosilane at reduced pressure (20 mTorr). PDMS was then cast onto the silicon, cured thermally (65 °C), and removed from the master. The PDMS replica contained the three-dimensional (3D) relief features in the silicon. These 3D relief features allowed patterning of narrower features than were possible using only standard lithography. Figure 2 shows an electron micrograph of the etched silicon and the corresponding scanning force micrograph of the elastomeric replica of the master.

This newly fabricated stamp was used again to pattern SAMs via μCP on Au/Ti (300 Å/300 Å) supported on gallium arsenide. Note that while the original stamp had a large pattern contact area (> 50%) and adhered spontaneously when placed on the surface of a gold film [1–3] the new stamp had a much smaller fraction for pattern contact (< 0.2%) and thus required the application of pressure to make contact with the substrate. The size of the features formed by μCP was determined by varying the pressure on the stamp while the stamp was in contact with the gold surface. A light pressure of approximately 1–3 g cm^{-2} was sufficient to pattern SAMs and to fabricate features with dimensions as small as 200 nm. A thicker layer of titanium (300 Å) was used when patterning GaAs

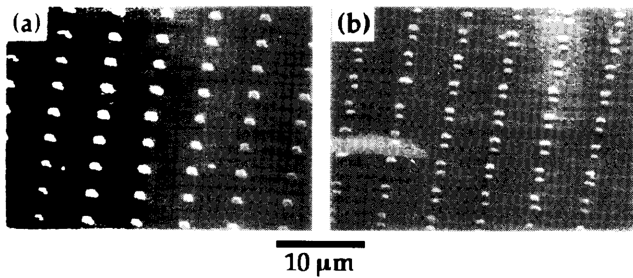

Figure 3. (a) Electron micrograph of a gold mask on GaAs, before cryoetching. (b) Electron micrograph of another sample after etching to 250 nm depth.

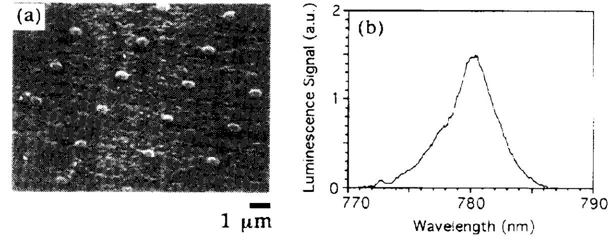

Figure 4. (a) Electron micrograph of MQW GaAs/AlGaAs after cryoetching using the Au/Ti mask. (b) Photoluminescence spectrum of MQW GaAs/AlGaAs after cyroetching to 220 nm depth, using the Au/Ti mask fabricated by μCP.

rather than the thin layer (10–50 Å) commonly used with silicon [1–5]. Here titanium served two functions: as an adhesion promoter between the gold and GaAs, and as a secondary resist to protect the GaAs from the gold-etchant solution. In order to transfer a pattern of SAM from gold to titanium to GaAs, two wet etching processes must be 'chemically' orthogonal: etchants for gold ideally should not affect the titanium layer and etchants for titanium should not damage either the gold or the gallium arsenide. Note that the gold layer was sufficiently thin so that it was not necessary to utilize an anisotropic etch. Thus an anisotropic etchant of an aqueous acidic solution containing an oxidizing agent (H_2O_2) was found to be a satisfactory etch for the gold [14].

In this connection, when etching gold in our previous work [1–5, 10, 11] we used basic solutions containing cyanide or ferricyanide. Under these conditions, however, the surface of gallium arsenide was damaged and roughened. Since gallium arsenide was more stable in a dilute acidic solution, we used an aqueous solution of thiourea, H_2O_2 and HCl (6 N) [14]. This etchant selectively removed the area unprotected by alkanethiolates. Although this etchant can, in principle, also remove the titanium layer, the etching action was stopped by removing the sample from the solution as soon as the gold layer was etched away. By varying the concentration of etchants and temperature of the solution, we found the optimum mixture for gold etchants to be a 10:1:1 (v:v:v) aqueous solution of 5% (w/v) thiourea, 15% (v/v) H_2O_2, and 6 N HCl at 35 °C. The exposed titanium layer was removed in an aqueous solution of HF (0.5%); HF did not affect gold but selectively removed Ti. This procedure left a generally good-quality GaAs surface, although some residual roughening of GaAs occurred.

Etch masks with features as small as 200 nm were fabricated using the stamps made from anisotropic etching of silicon. The Au/Ti pattern was subsequently transferred into the GaAs sample by cryoetching at 140 K in an atmosphere of Cl_2 (5 mTorr). The etching was activated by irradiation of the sample at 60 Hz repetition rate for 45 min using a 20 mJ cm^{-2} ArF laser (193 nm, 15 ns pulse width). This fluence did not significantly heat the sample surface [7]. Figure 3 shows electron micrographs of samples before and after etching to 250 nm depth; clearly, the pattern in the mask was faithfully transferred into the GaAs surface, indicating that the masks did retain their structural integrity during etching. The etched surface was generally of good quality, although it was somewhat rougher than that of samples patterned using conventional lithography and metal lift-off. This effect was most probably a secondary result of wet-etch residue on the sample surface or residual HF etching during the formation of the surface mask.

To test the suitability of this combination of processes for fabricating deep quantum features with submicrometer resolution, a gold mask patterned using μCP was used as a mask for cryoetching of MQW material. The substrate consisted three 5 nm GaAs quantum wells separated by 25 nm $Al_{0.3}Ga_{0.7}As$ barriers with a 5 nm GaAs gap, grown on a GaAs (100) substrate. This material was the same as used in previous experimental studies of etch-induced damage [9] and allowed direct comparison of results obtained here with those obtained using a different process of forming surface masks. The pattern in the Au/Ti layer was transferred into the MQW substrate by cryoetching. Figure 4(a) shows an SEM image of a sample after etching for 35 min ($\sim$ 220 nm etch depth); it shows that submicrometer resolution can be attained using the combination of μCP and cryoetching. The etching again left a somewhat rougher surface compared to etched samples patterned using conventional lithography and metal lift-off [8].

Photoluminesncence spectroscopy of the etched features was performed to ascertain the quality of the etched features and to detect any etch-induced near-surface damaged layer. While luminescence spectroscopy is not sensitive to all forms of etch-induced damage, it is a direct measurement of a sample's light-emitting ability, including the formation of nonradiative traps and centers such as seen in damage due to ion etching. The photoluminescence of the resulting quantum-well features was measured using 20 mW Ar^+ laser (20 μm spot beam), excited at 488 nm in a backscattering geometry (the excitation beam and luminescence collection are at right angles to the sample). Because the sample was etched beyond the depth of the quantum wells, the detected signal arose only from the quantum wells. After passing through a 0.85 m double spectrometer, the luminescence was detected by a photomultiplier tube in photon-counting configuration. The luminescence spectrum of the etched quantum features (figure 4(b)) showed strong luminescence and is comparable to that of a conventionally patterned sample. The absence of a large masked area, and, hence, unetched area on the sample makes it difficult to compare directly this luminescence efficiently to

that of the unprocessed material; however, based on the fill factor (0.014), mask thickness (300 Å Au/300 Å Ti), and features size (380 nm radius), we estimate the luminescence efficiency of these features to be similar to that of samples patterned using electron-beam lithography. Typically, features of this range of radius which are etched without bulk or near surface damage, but with unprotected walls, have shown a decrease in luminescence efficiency of approximately 100× of the unprocessed material due to nonradiative recombination on the sample side walls. The luminescence peak position and lineshape observed here are the same as that of the unprocessed material. Thus, these show that there is no significant etch-induced damage or degrading of the surface during the formation of the surface mask with μCP.

These results demonstrate that Au/Ti etch masks fabricated by μCP can be used successfully in a relatively corrosive etching of GaAs-based materials. In addition, μCP provides an alternative to conventional lithography in fabrication of masks having submicrometer features. Since μCP can be used to pattern different metals such as Au, Pt, Ag, and Cu, it should be possible to extend this process to fabricate etch masks using these metals or combinations of these metals. These techniques offer a method of rapidly fabricating a large number of high-quality submicrometer-scale features.

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