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Etching of Mesa Structures in HgCdTe

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Mesa structures were etched in HgCdTe using different Br_2/HBr/Ethylene glycol (EG) formulations. Etch rate and degree of anisotropy (A) were studied in detail for all of the combinations. Addition of EG to the conventional etchant gave $A > 0.5$, with controllable etch rates. Optimum etchant composition was determined to be 2% Br_2 in a 3:1 mixture of EG:HBr. This composition resulted in a good anisotropy factor of ~0.6 and a reasonably optimum etch rate of ~2.5 µm/min, with rms surface roughness of ~2 nm. Kinetics of the etching reaction have also been studied for the optimum etchant concentration and an etching mechanism has been proposed.

Key words: Wet etching, anisotropy, etching mechanism

INTRODUCTION

Third generation infrared detectors such as multicolor photodiodes and high operating temperature detectors are being fabricated to meet the requirements of high end thermal imaging systems. Two dimensional arrays of these detectors are fabricated by mesa etching isolation in the p-on-n , n-on-p, or multilayer HgCdTe epitaxial layers grown by molecular beam epitaxy (MBE) or liquid phase epitaxy (LPE). In order to retain high fill factor and to accommodate two or more detectors per pixel, a tight control over the device dimensions and a good control over mesa etching of HgCdTe is an important issue. Anisotropic dry etching processes have been used to realize the small geometries with a desired dimensional control.[1–3] Though some success has been reported in this direction, these etching processes induce lateral damage and alter the electrical and photo-electrical properties of HgCdTe layers.[4–6] The damages induced in the HgCdTe layers during dry etching can cause undesirable type conversion of the layer being etched or can create mobile defects,[7,8] thus causing thermal and temporal instability in the devices. The induced surface roughness forms high surface recombination surfaces/regions.[8,9] In order to remove the damage caused by the dry processes, wet etching techniques have to be employed finally. Wet chemical etching by using Br_2-HBr solution has been conventionally used for etching large pattern geometries in HgCdTe . Alcoholic solutions of Br_2 are generic wet etchants of II–VI compound semiconductors.[10] Although the wet etching process is isotropic, it does not induce undesirable changes in properties of HgCdTe. Wet etching is preferred over dry etching of high density mesa structures in HgCdTe for a fine control over the etching in lateral and vertical directions. Adding an etch rate controlling agent to the general etchant of HgCdTe is one promising approach. A viscous additive like ethylene glycol (EG) can serve the desired purpose. In order to improve the control over etching process for fabrication of high density HgCdTe detector arrays, EG has been added to Br_2-HBr solution. But the etching mechanism needs to be worked out before utilizing this mesa etching process for the fabrication of advanced detector arrays. It is also desirable to develop a reproducible etching process for achieving high anisotropy, good dimension control, low surface roughness, and desired edge profile. For this purpose, the effect of etchant composition and process temperature on etching of HgCdTe has been investigated. This paper reports the results of a systematic study on etching of mesa structures under different process conditions.

EXPERIMENTAL PROCEDURE

A four-level experiment was designed with different process parameters to cover the entire response space. The $Hg_{1-x}Cd_xTe$ wafers (x value of 0.28) used

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for the set of etching experiments were procured from M/S SMALL Enterprises, Ukraine. The wafers were diced with a wire saw and pasted on sapphire. Next, these wafers were mechanically lapped and polished with alumina powder of decreasing grit sizes. This was followed by chemomechanical polishing and a free etch in 0.1% Br_2 in methanol solution for 1 min. The polished HgCdTe surface was examined using Nomarski microscope and an ellipsometer (Gartner Scientific Inc., 6328 Å). It was ensured that the surface was free from oxides, damages, and contamination. Two photolithographic masks were used to replicate the detector dimensions. One of the masks had 600 μm long linear structures with a trench width of 50 μm, and the other consisted of two dimensional mesa structures separated by 30 μm trenches. The etchant used for these experiments is a mixture of Br_2 + HBr + EG. In phase I, different etchant formulations were used by varying the concentration of Br_2 from 1% to 3% at different levels. For each level of experiment with a particular Br_2 concentration, the fraction of EG in HBr was changed from 0 to 1. In phase II, a set of experiments was conducted by varying the process temperature from 5°C to 50°C for the optimum etching conditions determined in phase I. Surface roughness and variation in surface composition, due to the etching treatment, were analyzed by a Veeco Dektak[3] profiler and ellipsometry measurements. The etch rate and anisotropy were determined as a function of key process variables, namely, composition of etchant and its temperature. The vertical etch rate (R_V) was determined by measuring the etch depth using a Dektak profiler. Lateral etch rate (R_L) was determined by observing the undercut in the masked structures under a high magnification phase contrast microscope. The degree of anisotropy is defined as $A = 1 - R_L/R_V$. Reaction kinetics, for the optimum etchant composition, was determined by etching the masked HgCdTe wafers at different temperatures.

RESULTS AND DISCUSSION

Figure 1 is a plot of etch rate versus fraction of EG in HBr for different concentrations of Br_2 in the solution. The graph shows linear variation of etch rate with the etchant composition. It is apparent that the etch rate decreases as the amount of EG is increased in the mixture. Ethylene glycol increases the viscosity of solution and limits the availability of free Br_2 in the solution, which is evident from the mechanism of etching discussed later. Also, the etch rate is higher for a greater concentration of Br_2 in the solution. Etching proceeds by reduction of Br_2 at the semiconductor surface followed by oxidation of HgCdTe and subsequent dissolution of the reaction products.[11] Thus, the concentration of bromine ions in the solution controls the etch rate. The Br_2-HBr is used for etching HgCdTe photodetectors of large dimensions, but a high lateral etch rate leads to poor process control and a large undercut in the features. An optimum vertical and lateral etch rate with desirable anisotropy is needed for end point detection and dimensional control. Addition of EG to the etch solution increases its viscosity and has been found to slow the rate of reaction. Figure 2 illustrates the experimental values of anisotropy corresponding to the data shown in Fig. 1. Anisotropy is observed to be highest for 2% Br_2 in various ratios of HBr to EG. This is attributed to the smallest ratio of lateral to vertical etch rate for the particular compositions. For a particular concentration of Br_2, degree of anisotropy is greater for the composition with higher etch rate. An exception is higher concentration of Br_2 (3% or greater) in the etchant, where faster etch rate is not necessarily accompanied by a corresponding high A value. This is because high concentration of Br_2 in the solution accelerates the etch rate, so that the lateral etch rate becomes comparable to vertical and it becomes difficult to have a

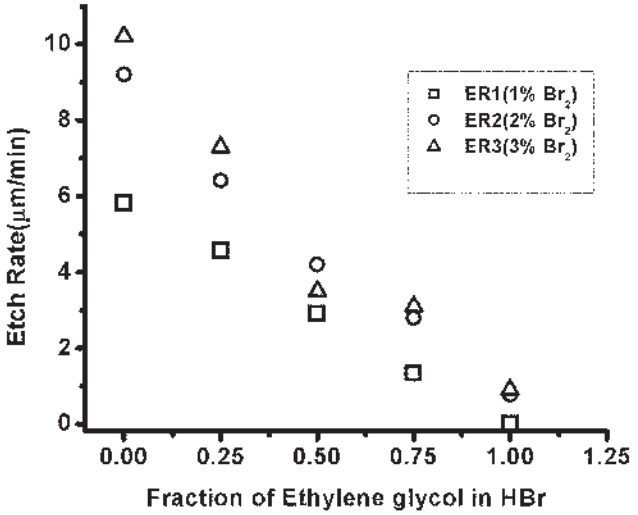

Fig. 1. Etch rate versus fraction of EG in HBr. The etch rate decreases linearly with concentration of EG in the solution.

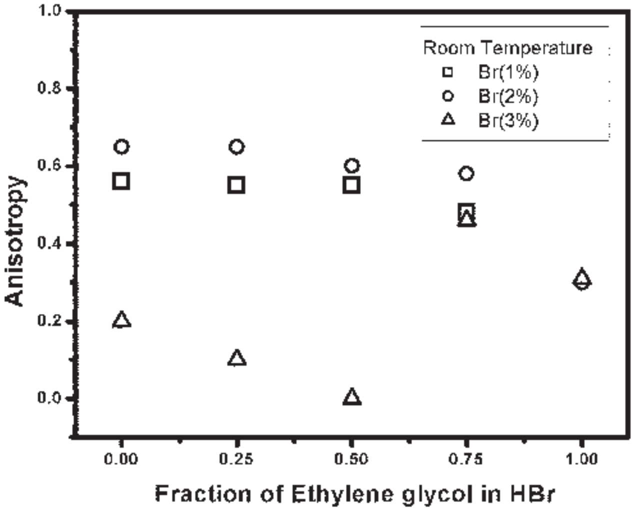

Fig. 2. Degree of anisotropy versus EG concentration in the solution at 21°C .

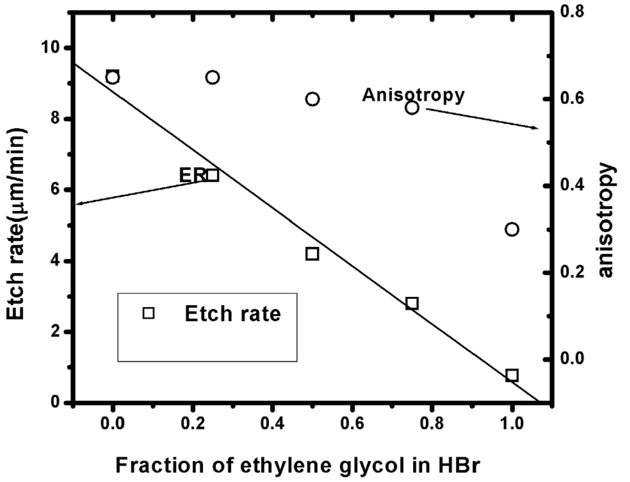

Fig. 3. Etch rate and degree of anisotropy (A) versus fraction of EG in HBr, for 2% Br_2 at 21°C. Few data points for etchant mixture of 3:1 EG/HBr and 2% Br_2 are also shown to study process variations.

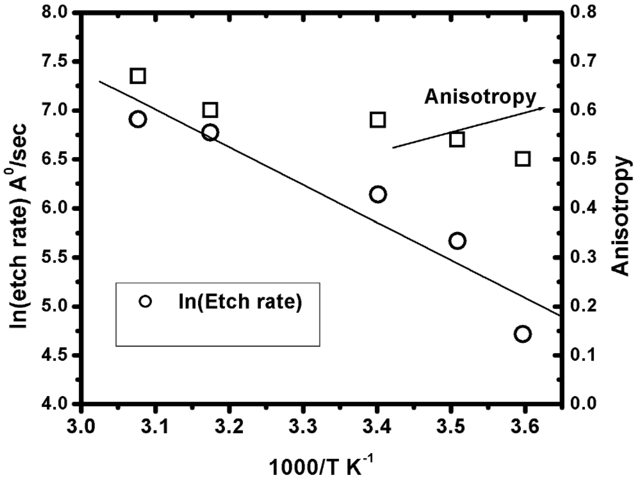

Fig. 4. Etch rate of HgCdTe in 2% Br_2 + 75%EG + 25%HBr as a function of temperature. Also shown is degree of anisotropy for these etching reactions, the faster the ER the greater is A.

process control. From the set of experiments it is evident that opting for too high Br_2 concentration is not favorable. Thus, etchant mixture of 2% Br_2 in various combinations of EG to HBr is suitable for the process. Figure 3 shows a plot of etch rate and anisotropy for 2% Br_2 in different ratios of EG to HBr. The variation in A is also shown and is not so sensitive to concentration of EG in the etchant. In fact, it is more sensitive to parameters such as photoresist thickness, area, and thickness of film.[12]

The primary objective of any etching process is to have a process with controllable rates having reproducible vertical and lateral etching over all surfaces of same type. For a particular set of conditions we should observe uniformity of etch depth, reproducibility of etched depth, and uniformity of pattern width. From the observations, it appears that the optimum combination should be an etchant formulation with low etch rate and degree of anisotropy better than 0.5. Etchant composition of 2% Br_2 in 3:1 ratio of EG to HBr is chosen as the optimum combination on the basis of all of the experimental observations. Few preliminary experiments were performed to investigate process uniformity using this etchant composition. The mean etch rate is 2.78 μm/min ± 26% variations while the average anisotropy is 0.63 ± 11% variations. These figures are in agreement with other wet etching processes.[12] Nonuniformity in etching can be mainly attributed to factors such as drift in concentration of Br_2 in the etchant, as it evaporates from the etchant quickly. A tight control over all the parameters and ability to sense exact time to endpoint, could give uniformity within ±10%. With increasing viscosity of the solution, the etch process tends to be diffusion controlled. Etch depth measurements show trenching at edges of photoresist (etch rate being faster there) with a convex profile in-between adjacent features. This is because the ions or molecules diffuse faster along the sidewalls than along a flat surface and hence, accelerate sidewall etching resulting in notched shapes.[3]

The kinetic parameters that affect the reaction rate are activation energy, agitation, viscosity of solution, concentration of solution, and crystallinity of the film.[12] The requirement for wet and dry etching to take place is that the reaction should be preferably exothermic; in addition, the transport mechanism also governs the kinetics of reaction. During both phases in the set of experiments, it is observed that the etchant concentration does not affect the etch rate. In the case of wet etching, an ample amount of liquid surrounds the wafer and the etchant concentration does not fall to a negligible value at the surface. Therefore, it is plausible that the process is limited by diffusion of reactants and products to and away from the surface, respectively. Agitation of the viscous solution helps in removal and transportation of the reaction products away from the surface. The purpose of adding a viscous additive to the etchant was to slow the reaction rate to a diffusion-limited process and to have a control over process uniformity. To get a better insight into kinetics of reaction, the activation energy of the process has been determined. Effect of process temperature on etch rate and anisotropy has been studied using etchant composition of 2% Br_2 in 3:1 ratio of EG to HBr. The results of these experiments are shown in Fig. 4. It is observed that the etch rate doubles with every 10°C rise in temperature and faster etching is accompanied with higher anisotropy. The activation energy for the reaction determined from Fig. 4 is ~7.5 kCal/mol, which corroborates the observation that the process is diffusion-controlled.

Figure 5 shows micrographs from scanning electron microscopy (SEM) of the mesa structures etched in HgCdTe using the optimum etchant composition at different temperatures. The figures clearly illustrate the sloped profile due to wet etching effects. The kind of slopes observed in Figs. 5a and b are

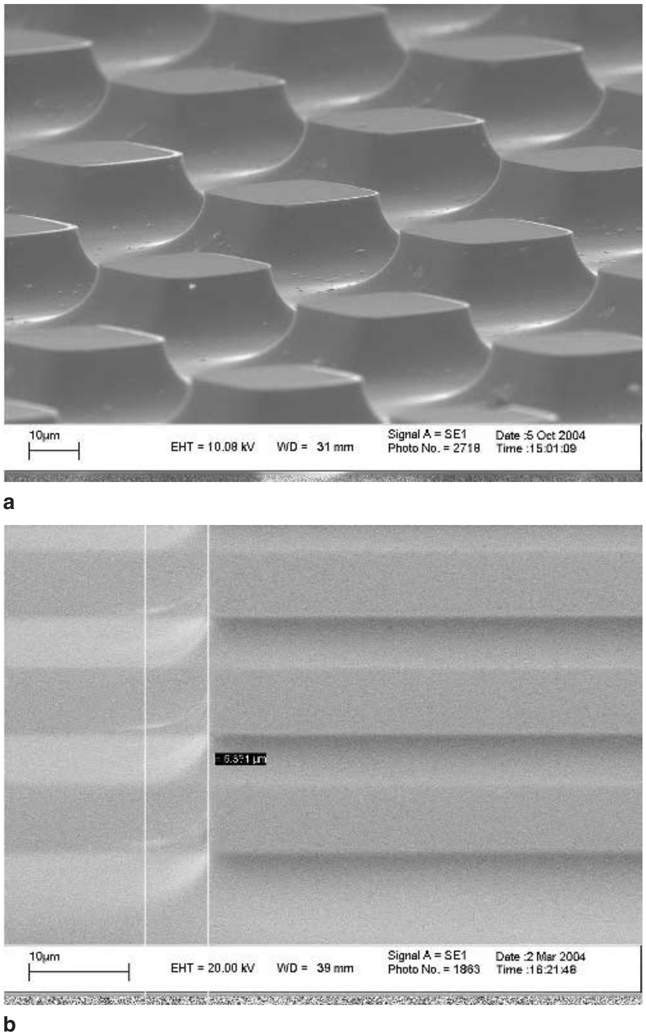

Fig. 5. Scanning electron micrographs of structures etched in HgCdTe using 2% Br_2. (a) SEM image of mesa etched at 21°C in 3:1 ratio of EG to HBr. (b) Etching in 2% Br_2 at low temperature (10°C). Lower etch rate results in good control over feature geometry.

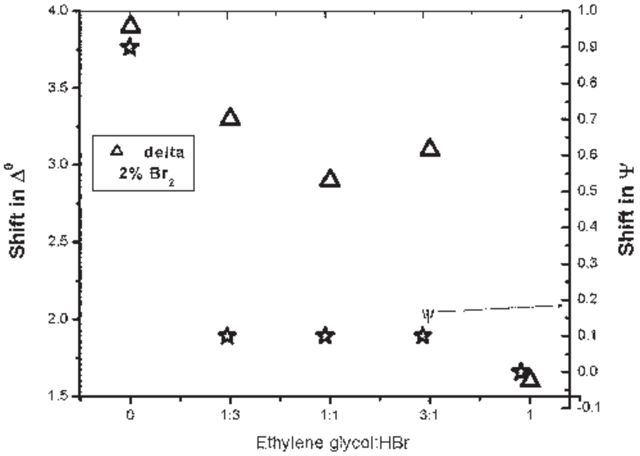

Fig. 6. Shift in ellipsometry parameters Δ and Ψ as a function of ratio of EG to HBr for 2% Br_2 .

preferred for metal coverage over the steps.[12] The edge profile can be tailored by varying composition of the etchant, temperature of solution, and photoresist parameters. At lower temperatures the mean free path of the diffusing species is large and hence, the tendency of fast etching at the corners is somewhat curbed. It is also observed that the features etched at low temperature, shown in Fig. 5b, have good control over the etched profile. Etching at high temperature resulted in ragged edges/sidewalls and the etchant was found to attack the photoresist. Low-temperature etching slows the reaction rate, giving better control over the feature profile. Low-temperature etching is found to yield consistent etch rates, since the wafer temperature was maintained constant. It also saves the photoresist during etching against thermal deterioration and flow.

Rough sidewalls can act as high recombination regions and cause performance degradation of the devices. Therefore, the etching process should leave behind clean and damage free sidewalls. A limited number of experiments were conducted to study the effect of etching conditions on roughness of the etched surface. The polished surface was exposed to these etching conditions and change in ellipsometry parameters and rms roughness was measured using profiler. Ellipsometry is a widely used optical method to estimate surface roughness and surface stoichiometric variations.[13] It is also used during various stages in our device fabrication process to set an acceptance window (for a known composition of HgCdTe) according to deviations in Δ and Ψ from initial values. Ellipsometric measurements recorded on a well-polished surface of mercury cadmium telluride (MCT) wafer served as a reference to study the etch-induced surface roughness and stoichiometric variations. The shifts in Δ and Ψ values from the corresponding reference data are shown in Fig. 6.

In summary, spatial variation in surface roughness averaged over three regions across the wafer varied from 2 nm to 7 nm, depending on the concentration of the etchant, being the least for highest concentration of EG in the etchant. Ellipsometry measurements indicated only a negligible change in Ψ that shows that surface composition has not changed during etching. However, a shift in Δ from 1.5° to 3.3° was recorded (Fig. 6). Shift in Δ value towards the lower side can be attributed to the change in surface roughness corresponding to different compositions of etchant.[13] Since no oxide layer was visible under the phase contrast microscope (Nomarski mode), the shift in Δ can be attributed to surface roughness. However, etching in Br_2/HBr only solution resulted in a shift in Ψ value by 0.9°, implies that the surface is probably Te rich for this composition of etchant. This is a qualitative analysis: better surface analysis can be done by techniques such as x-ray photoelectron spectroscopy (XPS) or Auger electron spectroscopy (AES).

MECHANISM OF ETCHING

Wet chemical etching of metals and semiconductors normally proceeds by oxidation (ionization of metals atoms) followed by transfer of electrons to a suitable reducing agent (reduction), and the reaction products are removed by a suitable solvent. The driving force for etching and dissolution is the change in free energy (ΔF) taking place during the reaction.[12] The ternary alloy HgCdTe is composed of pairs of group II–VI compounds HgTe and CdTe having the same type of crystal structure and chemical formula. Both components are reported to etch at different rates in acidic solutions.[14] Intermediate oxidative decompositions of HgCdTe in the etchant and the corresponding free energy changes, which could help in understanding the mechanism, are as follows:

$$\mathrm{CdTe} + 2\mathrm{h}^+ \rightarrow \mathrm{Cd}^{2+} + \mathrm{Te}^0 \quad \Delta F = 3.5\ \mathrm{kCal/mol} \tag{1}$$

$$\mathrm{CdTe} + 6\mathrm{h}^+ \rightarrow \mathrm{Cd}^{2+} + \mathrm{Te}^{4+} \quad \Delta F = 55.8\ \mathrm{kCal/mol} \tag{2}$$

$$\mathrm{HgTe} + 2\mathrm{h}^+ \rightarrow \mathrm{Hg}^{2+} + \mathrm{Te}^0 \quad \Delta F = 46\ \mathrm{kCal/mol} \tag{3}$$

$$\mathrm{HgTe} + 6\mathrm{h}^+ \rightarrow \mathrm{Hg}^{2+} + \mathrm{Te}^{4+} \quad \Delta F = 98.5\ \mathrm{kCal/mol} \tag{4}$$

It is seen from the free energy data that the component that will etch rapidly in an acidic ($\mathrm{pH} = 0$–6) solution is CdTe with etch rate of $\mathrm{Cd} > \mathrm{Hg} > \mathrm{Te}$. A strongly acidic solution ($\mathrm{pH} = 0$) may leave the etched HgCdTe surface richer in HgTe component.

Thus, although the Hg-Te bond is weaker than Cd-Te bond, CdTe sub lattice is less stable in wet etchants because of the lower free energy barrier.[14] The holes are produced by reduction and subsequent adsorption of free bromine molecules present in the $\mathrm{Br_2} + \mathrm{HBr} + \mathrm{EG}$ solution, on the HgCdTe surface as shown below. The adsorbed Br^- will react with tellurium anions on the surface to give negatively charged ions and neutral Te^0.[11]

$$\mathrm{Br_2} \rightarrow 2\mathrm{Br}^- + 2\mathrm{h}^+$$

$$\mathrm{Te}^{2-} + 2\mathrm{h}^+ \rightarrow \mathrm{Te}^0$$

$$\mathrm{Br_2} + \mathrm{Te}^{2-} \rightarrow 2\mathrm{Br}^- + \mathrm{Te}^0 \tag{5}$$

$$\mathrm{HBr} \rightarrow \mathrm{H}^+ + \mathrm{Br}^- \tag{6}$$

The Br^- anions dissolve Cd and Hg from the surface, forming soluble Cd and Hg bromides ($\mathrm{CdBr_2}$, $\mathrm{HgBr_2}$), which are removed by the solvent. The probability of formation of $\mathrm{TeBr_4}$ is small and leaves elemental tellurium. Gradually, an unstable Te sub lattice with Te^0 dangling bonds is retained and stresses develop at HgCdTe-Te interface favoring removal of Te in the form of atoms during etching. Thus, $\mathrm{Br_2}$ is the oxidizing species, while HBr serves the purpose of an acidic media responsible for dissolution of the oxides.

Another redox reaction possible in the solution resulting in formation of dibromoethane and water, in the presence of EG is[15]

$$\mathrm{CH_2OH - CH_2OH} + 2\mathrm{HBr} \rightarrow \mathrm{CH_2CH_2Br_2\,(aq)} + 2\mathrm{H_2O}$$

Hydrolysis of bromine in water is a possible reaction:

$$\mathrm{Br_2} + \mathrm{H_2O} \rightarrow \mathrm{HBr} + \mathrm{HBrO}$$

$$2\mathrm{HBrO} + \mathrm{Te}^{2-} \rightarrow \mathrm{TeO_2} + 2\mathrm{HBr} + 2\mathrm{e} \tag{7}$$

$$2\mathrm{HBrO} + \mathrm{Te}^0 \rightarrow \mathrm{TeO_2} + 2\mathrm{HBr} \tag{8}$$

This is a reaction which competes with formation of neutral Te in the presence of EG in the solution and hence, limits the etch rate. Ethylene glycol controls the reaction rate because extensive hydrogen bonding in the diol makes the solution viscous, and also limits the availability of free bromine (via formation of dibromoethane), thus increasing pH of the solution and lowering the etch rate. The reduced acidic nature of the solution due to the addition of EG increases the probability of formation of various oxides of the cations. On the basis of reactions 1–8, probable oxidation and dissolution reactions taking place during etching in the solution are:

$$\mathrm{Hg_{0.8}Cd_{0{\cdot}2}Te} + 2\mathrm{HBr} + 2\mathrm{HBrO} + \mathrm{Br_2} + 2\mathrm{CH_2OH\text{-}CH_2OH} \rightarrow 0.8\mathrm{HgBr_2} + 0.2\mathrm{CdBr_2} + \mathrm{TeO_2} + 2\mathrm{CH_2CH_2Br_2} + 4\mathrm{H_2O} \tag{9}$$

$$\mathrm{Hg_{0.8}Cd_{0.2}Te} + 3\mathrm{HBrO} \rightarrow 0.8\mathrm{HgTeO_3} + 3\mathrm{HBr} + 0.2\mathrm{CdTeO_3} \tag{10}$$

Finally, these reaction products get dissolved in the solvent (HBr).

CONCLUSIONS

An optimum wet etching process has been developed using a wet chemical etching approach to etch mesa structures in HgCdTe. Ethylene glycol has been added to $\mathrm{Br_2}$/HBr etchant for acquiring a better process control. Greater concentration of HBr in the solution results in a faster etch rate, and the higher the concentration of $\mathrm{Br_2}$, the greater is the etch rate. Addition of EG to the etchant resulted in structures having a degree of anisotropy (A) > 0.5 for all of the cases. The etchant composition of 2% $\mathrm{Br_2}$ in 3:1 EG to HBr was the optimum formulation in terms of a controlled etch rate of ~2.5 μm/min with A ≈0.6 and a better control over endpoint detection. Preliminary studies on run to run variations in etch rates and anisotropy showed a variation of 25%. However, these variations could be controlled through tight control over all the process parameters including etchant concentration. Surface roughness (rms) measured using a Dektak profiler and an ellipsometer varied from 2 nm to 7 nm , being least for 3:1 EG to HBr. No change in surface composition is apparent from ellipsometry data for $\mathrm{Br_2}$/EG/HBr etchant. However, etching in HBr /$\mathrm{Br_2}$ solution left a tellurium rich surface.

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