Scanning tunneling microscopy of etched HgTe/CdTe superlattices

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Scanning tunneling microscopy is demonstrated for determining the surface morphology of etched Hg-based semiconductors. Wet etching of HgTe/CdTe superlattices used a Br-based etch solution while dry etching used methyl-free radicals formed by electron cyclotron resonance in a reactive ion etching reactor. Both techniques produced smooth surfaces with random features over large regions. Features ranged in height from 1 to 5 nm for wet etching, while the smoothest dry etched sample had random features with an average height of 40 nm. Near mesa structures, evidence of differential etching was observed between the different composition layers in the HgTe/CdTe superlattices for both wet and dry etched samples. © *1995 American Institute of Physics.*

Devices based on HgTe/CdTe superlattices (SL) have many interesting predicted and measured properties.[1,2] Recent reports have provided experimental confirmation of many of these properties.[3,4] These SL structures have longer predicted[5] and measured[6,7] excess carrier lifetime compared to HgCdTe alloys of comparable band gap, opening the possibility of a new class of infrared light emitting structures. In addition, novel electronic effects are predicted due to quantum confinement in relatively large scale structures fabricated in Hg-based materials.[8] Dry etch processing is under investigation for such structures.[9]

Device fabrication in Hg-based materials typically involves etching mesa-type structures. Differential etching effects can arise when etching layered structure, particularly SL. By creating stepped or scalloped surface features, differential etching alters the effective surface composition thereby altering the properties of the device structures. If the CdTe layer etches faster, the increased HgTe fraction would lead to a smaller effective band gap and result in increased tunneling currents in devices. Differential etching on the mesa sidewalls will also complicate passivation. Thus, it is important to have knowledge of the microscopic effects of the etching process. This letter reports the first scanning tunneling microscopy investigation of the surface morphology of both wet and dry etched HgTe/CdTe SL surfaces, and present evidence for differential etching effects.

The HgTe/CdTe SL used in this etching study were grown at Martin Marietta's Electronics Laboratory using photon-assisted molecular beam epitaxy (MBE). Details are discussed elsewhere.[3] In brief, the superlattices consisted of multiple repeats of about 50 Å HgTe and 50 Å of CdTe. Mesa structures, 2 μm in height and ranging from 25 to 100 μm in diameter, were fabricated on the SL. The scanning tunnel microscope (STM) measurements were performed using a Nanoscope II instrument. The sample was exposed to air during the measurements and was placed on a micrometer stage that allowed precise positioning of the sample. All images were obtained in constant current mode. The scanning rate was chosen to be between 4 and 8 Hz, and the bias voltage ranged from 200 to 500 mV. A fixed tunneling current of 1 nA was used.

Chemical wet etching was performed using a proprietary Br-based etch solution. Control of microscopic roughness is accomplished by using etches which have a self-limiting mechanism which controls diffusion of the etchant to the surface, typically by forming a passive reactant overlayer that dissolves slowly in the solvent.[10] Ellipsometry measurements[11] indicate Br-based etching produces smooth surfaces for many binary semiconductors. However, our Br-based etch solution, optimized for HgCdTe, produced pronounced differential etching features when etching HgTe/CdTe SL structures. These features were easily observed using scanning electron microscopy as bands of different surface texture encircling the mesa structures.

The differential etching effect is related to the solubility of the reactant overlayer in the solvent. As guidance in obtaining conditions for minimum differential etching, etching studies were carried out on CdTe and HgTe single layers grown by MBE. Measurements at room temperature using our standard Br concentration indicated that CdTe etched at a slightly higher rate than HgTe. A systematic adjustment of Br concentration and solution temperature produced etch conditions that resulted in similar etch rates for both materials. No evidence of differential etching was observed by scanning electron microscopy for SL samples etched using the conditions in this intermediate regime. However, the etch studies indicated that the SL exhibited an etch rate that was about 30% lower than that measured for CdTe or HgTe single layers etched under equivalent conditions, indicating a modified etch chemistry.

The wet-etched sample exhibited features typical of isotropic etching. Mesa sidewalls were sloped with enhanced etching occurring near the base of the mesa. The etched surfaces appeared smooth and featureless when observed with both optical microscopy and scanning electron microscopy. STM was used to profile the microscopic morphology of flat

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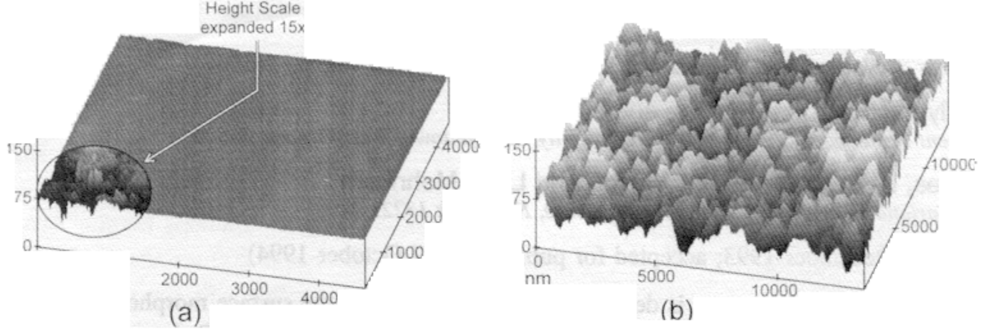

FIG. 1. Surfaces of HgTe/CdTe superlattices etched (a) with a Br-based solution and (b) using an improved ECR-RIE process. (a) This wet-etched area was located far from the mesa structures, and was quite flat over a large region. The surface features ranged between 1 and 5 nm in height. (b) The surface of this dry etched sample was relatively smooth over the entire sample, including the vicinity of the mesas. No evidence of differential etching was observed.

regions. The surface was reasonably smooth with randomly distributed features ranging in height between 1 and 5 nm, as shown in Fig. 1(a). This represents the first direct measurement of the microscopic roughness of a Br-etched Hg-based semiconductor surface.

The STM measurements revealed a periodic surface structure in the close vicinity of the mesas, as shown in Fig. 2. The 1 μm periodicity shown in Fig. 2 does not represent the actual SL layer thicknesses, but is representative of the SL intersecting the surface at a shallow angle. The periodic undulation observed with STM varied in height between 10 and 50 nm at different regions. The nearly equivalent thicknesses of HgTe and CdTe in the samples investigated preclude determination of which layer has the faster etch rate.

The difference in conductivity between CdTe and HgTe adds a complication to the interpretation. A different tunneling current may result from the individual layers due to conductivity differences, resulting in an apparent height variation. This effect has been reported for ceramic multilayer systems.[12] However, the significant variation in the measured heights of the periodic features is a strong indication of differential etching. At worst, these numbers can be viewed as an upper bound on differential etching effects.

Electron cyclotron resonance reactive ion etching (ECR-RIE) can produce the highly anisotropic etching desired for close geometries. Studies indicate that ECR-RIE etching produces stoichiometric surfaces in HgCdTe alloys,[13] and allows nanometer scale fabrication.[9] A recent study of GaAs indicated that ECR-RIE etching produced the lowest sidewall damage levels of any energetic dry etch process.[14] These desirable features led to the investigation of ECR-RIE etching of HgTe/CdTe SL.

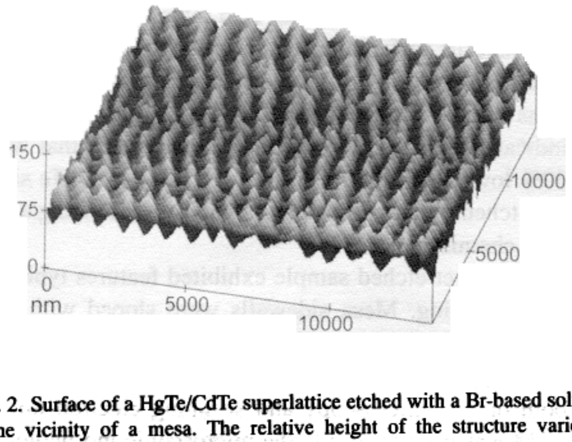

FIG. 2. Surface of a HgTe/CdTe superlattice etched with a Br-based solution in the vicinity of a mesa. The relative height of the structure varied at different regions of the sample, consistent with differential etching.

Dry etching was performed in a PlasmaQuest ECR reactor system equipped with an Astex 2.45 GHz ECR source. The smoothest surfaces resulted when a 4% hydrogen in argon gas mixture was introduced into the ECR source, while a 10% methane in argon mixture was fed into the main process chamber downstream of the ECR source. A rf bias at 13.56 MHz was added to the sample chuck to allow ion etching to control etch rate and anisotropy. Conditions used for the HgTe/CdTe SL etching were typically 3–4 mTorr pressure, 750 W microwave power, and 50 W rf power.

Dry etching requires the formation of sufficiently volatile species through reaction with gas phase enchants. In HgCdTe, the etching is believed to proceed via the reaction[15]

$$\mathrm{HgCdTe}+4\mathrm{CH_3}+2\mathrm{H}\rightarrow\mathrm{Hg(CH_3)_2}+\mathrm{Cd(CH_3)_2}+\mathrm{TeH_2}.$$

A desorption-limited etch mechanism results if reactant products have a low volatility. The limiting etch products are believed to result from the group II constituents.[16] Conventional enchants such as Cl, F, or H form low volatility compounds with Cd,[13,17] resulting in reduced etching. Although more volatile, $\mathrm{Cd(CH_3)_2}$ may still be the limiting species. Thus, the different compositions in layered structures can result in reactant products with different volatility and lead to differential etching effects as observed in RIE etching between HgCdTe epilayers and CdTe buffer layers grown on GaAs.[15] Ion bombardment enhances reactant volatility[18] and can reduce this effect. Methane can also form a hydrocarbon layer on the etched surface. Hydrocarbon layers on mesa sidewalls serve as an etch stop and promote anisotropy.[9] The highly directional ion impingement used in RIE removes this hydrocarbon layer on perpendicular surfaces, promoting anisotropic etching.

The first dry etched sample investigated was etched in the afterglow mode,[13] where ion impingement is minimized and etching is due to methyl radicals and hydrogen ions only.

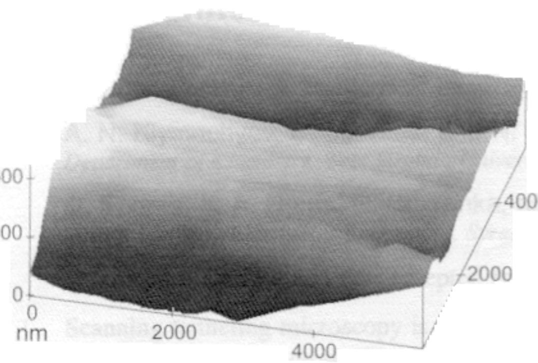

FIG. 3. Surface of a HgTe/CdTe superlattice etched using ECR/RIE under nonoptimal conditions. This surface was very rough, and many periodic features were observed on the sloped surfaces. This STM scan represents two periods of a structure due to severe differential etching were the SL intersects the surface.

A qualitative description of the surface would be "spongelike" due to the amount of texture, with many irregular features on the surface. The operating conditions were consistent with the formation of hydrocarbon overlayers. Thus, the observed highly nonuniform etching is likely due to hydrocarbons serving as etch stops in an uncontrolled fashion.

By the addition of a rf bias, ECR-RIE produced highly anisotropic etching in the HgTe/CdTe superlattices similar to HgCdTe.[9,15,17] The sidewalls of the mesa were nearly perpendicular. The etched surface appeared smooth when observed by optical and scanning electron microscopes. The second dry-etched sample was one of the first etched in the ECR-RIE configuration. It still exhibited a large degree of surface texture. Periodic structures were superimposed on the larger background surface texture. Differential etching was more pronounced than in the wet-etched case. Figure 3 shows two periods of this feature, typical for this sample. The height variation increased by nearly a factor of 10 over the wet etched case, to about 200 nm. The large increase in differential etching over the wet etch case indicates such effects are important in dry etching of SL structures.

The third dry etched sample represented the end product of a series of experiments to provide smoother surfaces using ECR-RIE. STM investigations indicated a remarkably improved surface over the previous dry etched samples, as depicted in Fig. 1(b). A surface texture was present with random height variations on the order of 40 nm. Importantly, no evidence of differential etching was found on this sample. This is a pronounced difference from *all* the other samples examined in this study implying there is an absence of differential etching. Thus, ECR-RIE can be optimized to minimize differential etching effects in HgTe/CdTe SL structures. However, differential etching may be present on the mesa sidewalls, where the effect of RIE is minimized.

In conclusion, this study has established that STM provides valuable information concerning microscopic surface morphology resulting from chemical etching on a scale inaccessible with optical or scanning electron microscopy. Wet and dry etching can produce smooth surfaces on Hg-based semiconductors. The wet-etched sample exhibited the microscopically smoothest surface, with features ranging between 1 and 5 nm in height. Dry etching relying only on the reactivity of the chemical species without ion etching produced a highly textured, spongelike surface.

Both wet and dry etched samples exhibited differential etching, where the SL structure intersects the surface. A periodic variation was observed on the wet etched sample that indicates height variations ranging between 20 and 50 nm, with variations of 200 nm observed on a dry etched sample. Additional studies will focus on the underlying chemical mechanisms, and attempt to arrive at a control strategy.

The best ECR-RIE sample exhibited a microscopically smooth surface, with random surface features about 40 nm in height. Indications of differential etching were absent. Further optimization can produce smoother surfaces, rivaling that obtained by wet etching with Br-based solution. The surface morphology measured in this study, when combined with the anisotropic etching provided by ECR-RIE, indicate that this will become the preferred etching technique for HgTe/CdTe SL devices and that STM will be effective for optimizing etch conditions.

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