The Effects of Hydrogen Bromide and Argon-Hydrogen on the Plasma Processing on the Surface Structure of HgCdTe

A. J. Stoltz[1], E. P. G. Smith[2], J. D. Benson[1], J. B. Varesi[1], G.M. Venzor[2], M. Devre[3],J. I. Shin[3], P. R. Boyd[4], and J.H. Dinan[1]

1 - U. S. Army RDECOM CERDEC NVESD
2 - Raytheon Vision Systems, Inc.
3 - Unaxis USA, Inc.
4 - U. S. Army Research Laboratory

Keywords: ICP, ECR, HBr, HREED, HgCdTe,

Abstract

Argon/hydrogen gas chemistry has been the basis for HgCdTe and CdTe plasma processing. This paper examines the effects that Argon/hydrogen plasma hav te on the crystalline surface structure of HgCdTe, CdZnTe, and CdTe using in-vacco Reflection high energy electron diffraction (RHEED). This paper also examines the effects that HBr, since the wet chemical etching of HgCdTe systems is based on bromine, in an attempt improve flexability of HgCdTe and CdTe plasma processing.

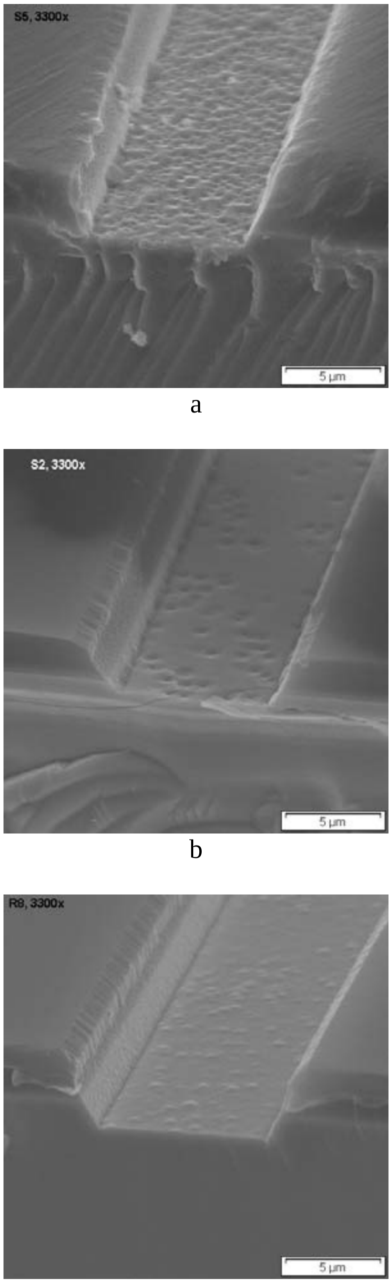
INTRODUCTION

Low Pressure-high density plasmas have been used to process several semiconductor systems, including group IV and compound semicondutors.[1-4] The primary gas chemistries used to dry process HgCdTe and CdTe have been argon/hydrogen and argon/hydrogen/methane based.[5-12] Reticulation of planar HgCdTe epilayers is a fundamental step in the fabrication of imaging focal plane arrays. Multi-color detectors and avalanche photodiodes require deep isolation trenches to preserve high fill factors. Although these chemistries have been used successfully to process greater than 5:1 ratio antisotropic trenches and used in the production of devices, greater flexibility is needed.[7] Since the wet chemical etching of HgCdTe systems is based on bromine, we have added HBr to the plasma process in an attempt improve flexability of HgCdTe and CdTe plasma processing.

To further understand the affects of plasma processing on HgCdTe Reflection high energy electron diffraction (RHEED) and in-situ spectroscopic ellipsometry (SE) will be utilized to observe changes in HgCdTe surface composition and crystallinity as a function of plasma gas chemistry and d.c. bias input power.

EXPERIMENTAL AND DISCUSSION

In this study HBr is examined as a stock gas in the (inductively coupled plasma) ICP plasma processing of HgCdTe. The starting material was longwave, cutoff ~10.5 micron, HgCdTe grown on Si.[13] Several concentrations of HBr are mixed in argon and argon/hydrogen gas chemistries, from pure HBr to just under 15% HBr in argon/hydrogen. The etch rate of these mixtures are shown in Table 1. The argon/hydrogen process has an etch rate of 0.24 microns/min., while the argon/hydrogen/hydrogen bromide processes exhibit etch rates between 0.17 and 0.13 microns/min. The etch rates of argon/hydrogen bromide based processes was 0.13 and 0.09 microns/min. The surface roughness is also dependent on the gas chemistry of the plasma. The addition of HBr allows for a wide variation of surface features as shown in figure 1. The starting material had an rms roughness of 2.29nm. Pure HBr leaves the surface of the HgCdTe very rough optically, with an rms value of 9.46 nm The best visual surface morphology are shown in figures 1b and 1c with mixtures of 16 sccm of Ar, 8 sccm of H2, and 16 sccm of HBr, and 16 sccm of Ar and 16 sccm of HBr respectively. These same etches correspond to the best measured root mean square roughness as determined by optical interferometry, (1.86 nm and 1.77 nm respectively). This is much smoother than the 51.7 nm roughness measured with the conventional argon/hydrogen plasma. These results, though preliminary, suggest that the addition of HBr to the conventional gas chemistry may improve plasma processing dramatically.



a

b

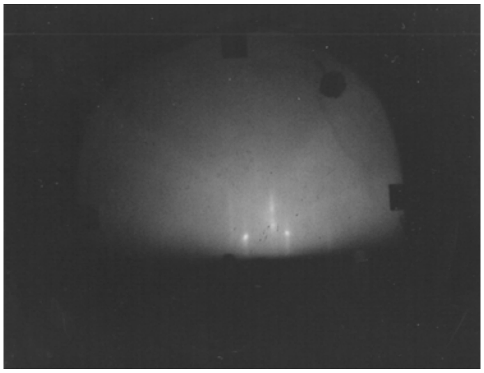
c

Figure 1. Scanning Electron Microscopy of HgCdTe processed with different concentrations of Ar, H_2, and HBr. A) 32 sccm of HBr, B) 16 sccm of Ar, 8 sccm of H2, and 16 sccm of HBr, and C) 16 sccm of Ar and 16 sccm of HBr.

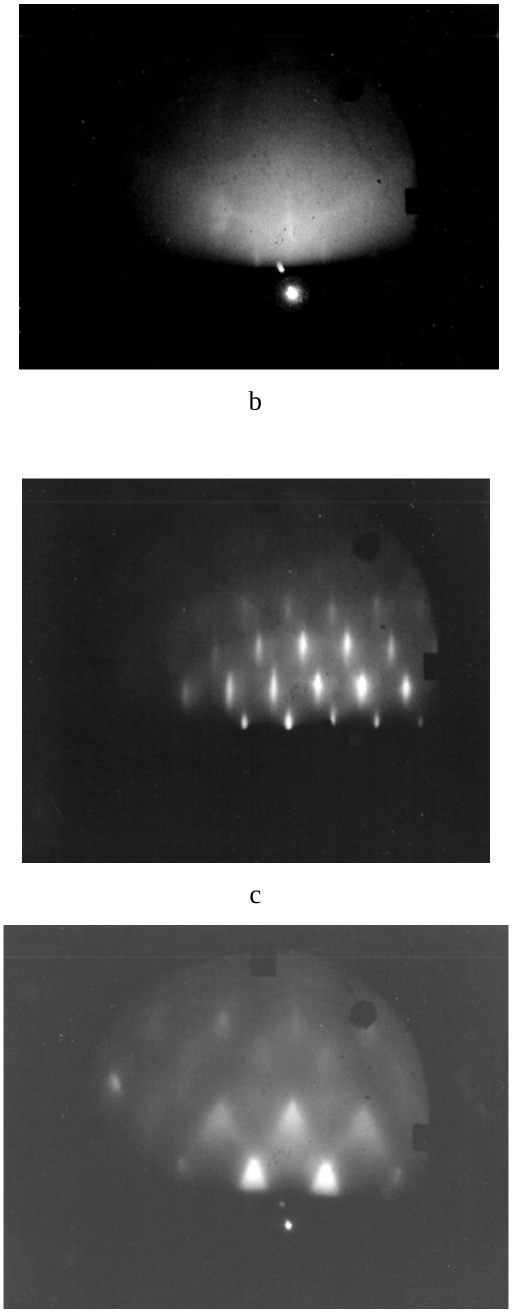
To further understand the effects of plasmas on HgCdTe, surface crystallinity is examined. Sputter theory predicts the nature and extent of the damage in semiconductor etching. For low energy noble gas sputtering, damage depths are comparable to the projected ion range. Kalbitzer and Oetzmann[14] empirically derived a formula relating the ion energy with the projected ion range. Using their formula, the damage depth for 15.2 eV (average ion energy for NVESD's 60W Electron Cyclotron Resonance (ECR) etch[15]) Ar ion bombarded HgCdTe is approximately 6 nm. Unlike III-V materials, amorphous surface layers are not typically observed in sputter etching II-VI semiconductors. The lack of an amorphous layer is attributed to recombination of defects due to the low binding energies and high iconicity of II-VI semiconductors. Extended defects (dislocation loops) and faceting are often observed in sputter etched II-VI materials.

For this study (211) HgCdTe deposited by MBE was ECR etched and then analyzed by RHEED and in-situ SE. These techniques should sample only the damaged surface region. RHEED is extremely surface sensitive with the crystallinity of the top ≈1nm probed. As seen in Figure 2 'a' and 'b', a diffuse RHEED pattern is observed before ECR etching. The diffuse RHEED pattern is likely due to a carbon and oxygen contamination layer created in the sample removal and re-mounting step. The contamination layer makes definitive RHEED analysis of the ECR etched surface problematic. RHEED images after ECR etching (Figure 2 'c' and 'd') show single crystalline HgCdTe. Although no amorphous surface layer is detected - faceting and twinning are observed.

The RHEED and SE experiments will be extended to determine the extent and type of damage caused by varying the ECR gas chemistry as well as the d.c. bias. The sample removal and re-mounting step will be eliminated thereby enhancing RHEED and SE analysis capability.



a



b

c

d

Figure 2. RHEED images from HgCdTe before (a and b) and after (c and d) 60W ECR etching. RHEED patterns ‘a’ and ‘c’ along the $[01\bar{1}]$ azimuth and ‘b’ and ‘d’ along the $[\bar{1}11]$ azimuth.

CONCLUSIONS

RHEED images after ECR Argon/Hydrogen plasma show single crystalline HgCdTe. Although no amorphous surface layer is detected - faceting and twinning are observed.

Adding HBr either argon or argon/hydrogen in an ICP process produces HgCdTe surfaces, less than 2.0 nm roughness, smoother than ICP argon/hydrogen only process. These results, though preliminary, suggest that the addition of HBr to the conventional gas chemistry may improve plasma processing dramatically.

REFERENCES

1. Suzuki, K., Ninomiya, K., Nishimatsu, S., and Okudaira, S., *J. Vac. Sci. Technol. B*, **3**:1025 (1985)

2. C. R. Eddy, Jr., D. Leonhardt, S. R. Douglass, V. A. Shamamian, B. D. Thoms, and J. E. Butler, J. Vac. Sci. Technol. **A, 17**(3), 780 (1999).

3. Seongsoo Jang and Wonjong Lee, J. Vac. Sci. Technol. **A, 19**(5), 2335 (2001)

4. John B. O. Caughman II and Willam M. Holber, J. Vac. Sci. Technol. **A, 9**(6), 3113 (1991)

5. P. O’Dette, G. Tarnowski, V. Lukah, M. Krueger, and P. Lovecchip. J. Electronic Mat. 28, 821 (1999).

6. A.J. Stoltz, J.D. Benson, Mason Thomas, P.R. Boyd, M. Martinka, and J.H. Dinan, J. Electronic Mater. **31**(7), 749 (2002)

7. A. J. Stoltz, J. D. Benson, P. R. Boyd, J. B. Varesi, M. Martinka, A. W. Kaleczyc, E. P. Smith, S. M. Johnson, W. A. Radford, and J. H. Dinan, J. Electronic Mat. **32**(7) 692, (2003).

8. E. P. G. Smith, J. K. Gleason, L. T. Pham, E. A. Patten, and M. S. Welkowsky, J. Electronic Mat. **32**(7) 816, (2003).

9. E. P. G. Smith, L. T. Pham, G. M. Venzor, E. M. Norton, M. D. Newton, P. M. Goetz, V. K Randall, A. M. Gallagher, G. K. Pierce, E. A. Patten, R. A. Coussa, K. Kosai, W. A. Radford, L. M. Giegerich, J. M. Edwards, S. M. Johnson, S. T. Baur, J. A. Roth, B. Nosho, T. J. DeLuon, J. E. Jensen, and R. E. Longshore, J. Electronic Mat. **33**(6) 509, (2004).

10. J. Baylet, O. Gravrand, E. Laffosse, C. Vergnaud, S. Ballerand, B. Aventurier, J. C. Deplanche, P. Ballet, P. Castelein, J. P. Chomonal, A. Million, and G. Destefanis, J. Electronic Mat. **33**(6) 690, (2004).

11. R. C. Keller, H. Zimmerman, M. Seelmann-Eggebert, and H. J. Richter, J. Electronic Mater., 25(6), 1270 (1996)

12. R. C. Keller, H. Zimmerman, M. Seelmann-Eggebert, and H. J. Richter, J. Electronic Mater., 26(6), 542 (1997)

13. N. K. Dhar, P. R. Boyd, M. Martinka, J. H. Dinan, L. A. Almeida, and N. Goldsman, J. Electronic Mater., 29(6), 748 (2000)

14. S. Kalbitzer and H. Oetzmann, “Ranges and Range Theories,” Radiation Effects **47**, 57 (1980).

15. J. D. Benson, A. J. Stoltz, J. B. Varesi, M. Martinka, A. W. Kaleczyc, L. A. Almeida, P. R. Boyd, and J.H. Dinan, “Determination of the Ion Angular Distribution for ECR Plasma Etched HgCdTe Trenches,” to be published J. Elec. Mat. **33** (2004).

ACRONYMS

MBE: Molecular Beam Epitaxy
ICP: Inductively Coupled Plasma
RHEED: Reflection High Energy Electron Diffraction
SE: Spectroscopic Ellipsometry
ECR: Electron Cyclotron Resonance