Improved Determination of Matrix Compostion of $Hg_{1-x}Cd_xTe$ by SIMS

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Results are presented to show an improved method for composition characterization of HgCdTe heterostructure using secondary ion mass spectroscopy. This method utilizes the molecular ions CsM^+ rather than $M^{\pm}$ ions. The advantage is that the molecular CsM^+ ion yield, unlike the atomic $M^{\pm}$ ions, is quite insensitive to the matrix material from which they are emitted. Composition of multilayer HgCdTe structure can be determined with excellent accuracy and depth resolution. Layer thickness of HgCdTe heterostructure can also be calibrated.

Key words: Composition analysis, heterostructure layer thickness calibration, HgCdTe, secondary ion mass spectrometry (SIMS)

INTRODUCTION

The increasing complexity of advanced HgCdTe heterostructure devices requires improved analytical capability for compositional characterization of the material. Some of the techniques used to determine the HgCdTe composition include infrared spectrometry, electron microprobe analysis, glow discharge mass spectrometry and x-ray diffraction analysis. Despite the good accuracy of these methods, they are essentially bulk measurement techniques, limiting their use for characterization the composition of multilayer structures.

Secondary ion mass spectrometry (SIMS) is a chemical analysis technique that employs mass spectrometry to analyze solid samples. The advantage of SIMS is that its depth profiling capability not only can provide accurate composition analysis but also can monitor the changes in composition with respect to sample depth. Other methods, such as Rutherford backscattering spectrometry (RBS), Auger electron spectroscopy (AES), and x-ray photoelectron spectroscopy (XPS) can also be used to perform composition depth profiles. However, RBS does not have sufficient depth resolution and AES and XPS are not economical for measuring the thicker multilayer HgCdTe structures.

We propose an improved analytical technique to determine $Hg_{1-x}Cd_xTe$ composition using SIMS. This method utilizes the molecular ions CsM^+ rather than $M^{\pm}$ ions (where M is the matrix element and Cs is the primary ion source). The CsM^+ ion yield have been observed to be quite insensitive to the matrix material from which they are emitted. The analysis method utilizing CsM^+ molecular ions for composition analysis, first reported in 1988,[3] is now a well-established method for stoichiometric analysis of III-V compound semiconductors and have been expanded to other materials including II-VI compounds.[4]

In a SIMS analysis, the sputter removal rate is dependent on the physical and chemical feature of the sample itself. In order to reflect the actual thickness of each compositional layer for a multi-layered heterostructure in a SIMS depth profile, a correction

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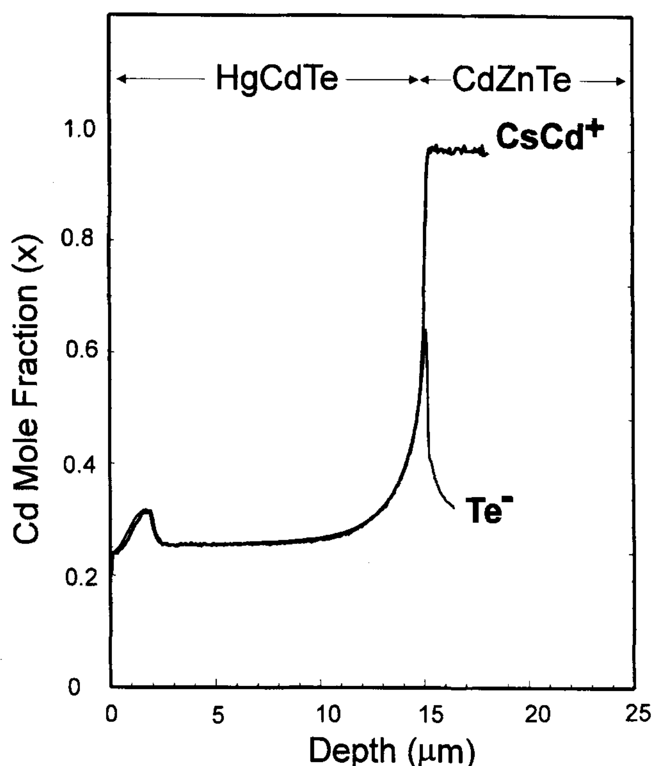

Fig. 1. Secondary ion mass spectrometry depth profile monitoring Te^- changes as a function of depth. The variation in the Te^- secondary ion intensities is an ion yield effect due to ionization efficiency variations and sputtering yield changes in the sputtering process related to the changes in the $Hg_{1-x}Cd_xTe$ composition, rather than the change of Te atomic concentration in the sample. The drop of Te^- signals in the CdZnTe substrate is due to sample charging effects. This charging effect is not shown when the sample was measured by monitoring the $CsCd^+$ ions. Accurate calibration of the HgCdTe composition can be performed using CdZnTe composition as reference when the CsM^+ technique is used.

for the difference in the sputter rate of each matrix composition must be made to the SIMS data. We have evaluated the SIMS sputter rate for different HgCdTe compositions and derived a relationship between HgCdTe composition vs sputter rate of each composition.

EXPERIMENTAL

Analyses were performed on a CAMECA IMS-4f double focusing magnetic sector instrument. The samples are bombarded by a focused energetic Cs^+ primary ion beam with a current of about 100 nA and a net impact energy of 5.5 keV. The stability of the primary current is within 1% over the course of each secondary ion mass spectrometry depth profile. The beam is rastered over a square area, usually a few hundred microns on a side to provide uniform primary ion current density over the secondary ion extraction area of the sample. Secondary ions formed during the sputtering process are accelerated away from the sample surface by a nominal sample voltage of 4500 V. A fraction of the secondary ions are accepted for analysis by a mass spectrometer and are collected from a circular image area centered in the rastered region.

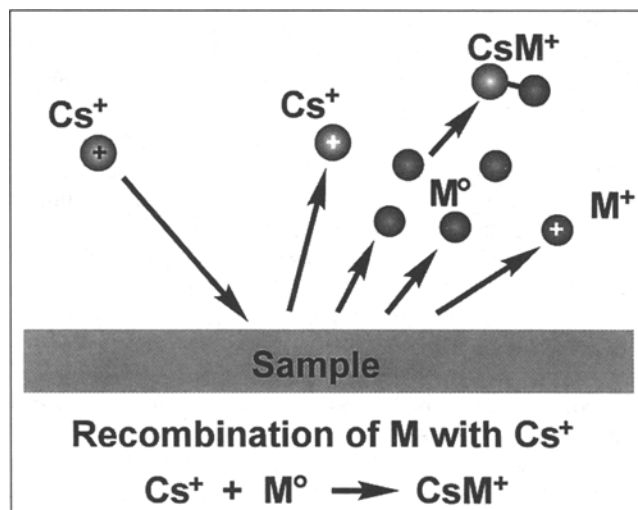

Fig. 2. Schematic drawing of the formation of CsM^+ molecular ions. The CsM^+ ions are assumed to be formed by a recombination process on the sputtered surface of the sample. The Cs^+ ions are supplied by the bombarding primary beam, which are implanted into the sample top surface region. The recombination of the sputtered neutral atoms M with the Cs^+ supplied at the top surface into CsM^+ are generated by the subsequent sputtering process.

RESULTS AND DISCUSSION

Ion Yield Variation (SIMS Matrix effect)

Application of SIMS to quantitative analysis of the composition of materials is limited by the accuracy of determination of the major elements. This problem is largely due to the extreme variations of the ionization probabilities of secondary ions, particularly their dependence on matrix composition (matrix effect). The ion yield variation is a function of the electronic (and vibration) states of both the sputtered species and the sample surface as well as the chemical bonding of the species to the surface. The secondary ion intensity, I_M, for an element M can be described by the following relationship:

$$I_M \propto \beta_M y C_M$$

where β_M = ionization probability (secondary ion yield), y = total sputter yield, and C_M = concentration of species M.

The β_M can vary by several orders of magnitude in different matrices whereas the variation of y with composition is much smaller (<10). This huge variation of the ionization probability is a serious obstacle for accurate quantitation by SIMS analysis.

Figure 1 shows a profile of Te monitored as its negative secondary ions using Cs^+ primary beam bombardment. The variation in the Te^- secondary ion intensities is an ion yield effect due to ionization efficiency variations, sputtering yield changes, and sample charging in the sputtering process related to the changes in the $Hg_{1-x}Cd_xTe$ composition, rather than the change of Te atomic concentration in the sample.

Composition Analysis

A SIMS technique developed for the compositional

analysis[1,2] takes the advantage of the matrix-induced variation in Te^- secondary ion yield in $Hg_{1-x}Cd_xTe$. This method, capable of providing compositional characterization with good depth resolution, is still an indirect method. Factors that may affect the Te^- secondary ion yield include surface topography, changes in sputter rate, fluctuations in primary beam stability, and high levels of dopants or other impurities. Since the Te^- ion yield variation is dependent on a combination of factors, no adequate normalization can be performed; therefore, the accuracy depends on these factors and thereby prone to run to run error. These artifact induced Te^- variation other than matrix composition change can seriously affect the accuracy of this method.

The insensitivity of the CsM^+ molecular ions to matrix effects makes it an ideal technique for measuring matrix composition changes, which will be unaffected by the artifacts produced by ion yield variations. Although the CsM^+ molecular ions have a much lower ion yield than atomic ions (with the exception of a few elements such as Ar, Zn, etc.), low yield is not a problem for measuring matrix components.

The CsM^+ ions are believed to be formed by a recombination process on the sputtered surface of the sample. The Cs^+ ions are supplied by the bombarding primary beam which are implanted into the sample top surface region. The recombination of the sputtered neutral atoms M with the Cs^+ supplied at the top surface into CsM^+ are generated by the subsequent sputtering process (Fig. 2). The probability of a recombination of the sample's atoms with the Cs^+ back-scattered from the surface is negligible because of the very low back-scattering coefficient of the Cs primary ions under normal SIMS analytical conditions. The recombination of the sputtered neutral atoms M with the high density Cs^+ will dominate the process. Hence, the detection of the CsM^+ ions would correspond to that of the sputtered atoms of the M element, making the analysis independent of the matrix effect. For a detailed discussion on the formation mechanism of the CsM^+ molecular ions, please refer to Gao et al.[5]

We have applied this technique to develop an independent means of quantitation of the $Hg_{1-x}Cd_xTe$ composition. A set of samples with different compositions ranging from $Hg_{0.8}Cd_{0.2}Te$ to CdTe were analyzed using Cs^+ primary beam bombardment. The molecular ions $CsCd^+$ and $CsTe^+$ were monitored. The $CsCd^+$ ion intensities were normalized to the $CsTe^+$ ion intensities to correct for the ion yield variation due to sputter rate changes related to composition differences. This normalization will also correct for the ion yield variation due to sample charging as shown by the Te^- profile in Fig. 1. The charging effects is also more severe in the negative secondary ion mode than that in the positive secondary ion mode for SIMS analysis.

A linear relation between the normalized $CsCd^+$ ion

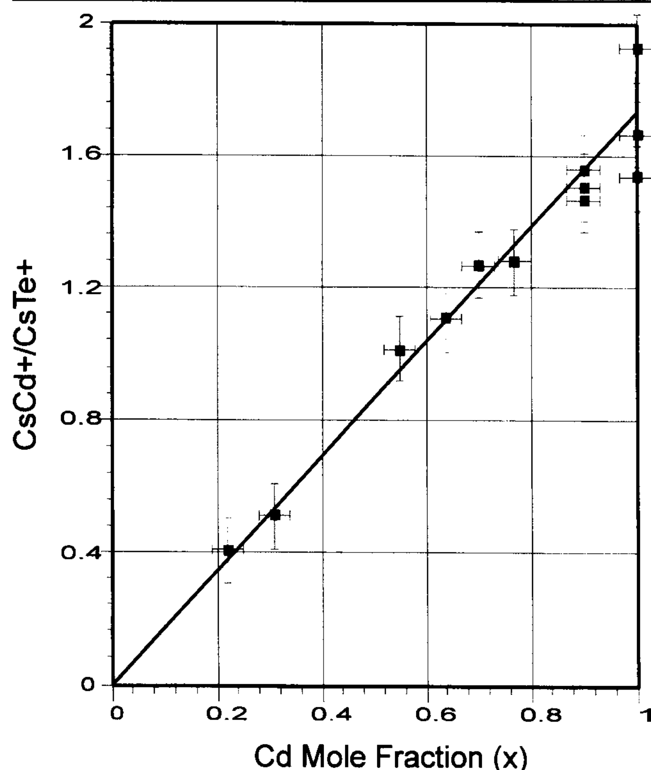

Fig. 3. A linear relation between the normalized $CsCd^+$ ion yield and x-value is established by correlating the $CsCd^+$ ion yield, normalized to the $CsTe^+$ ion yield, with $Hg_{1-x}Cd_xTe$ layers of known composition. The data is derived with samples from various sources. Error bars are based upon repeat measurements of samples of each nominal composition.

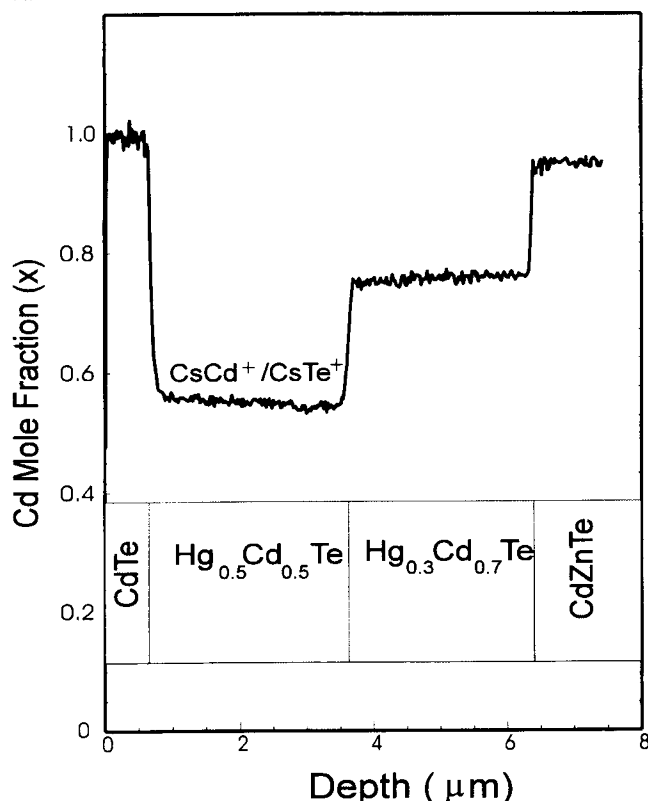

Fig. 4. SIMS depth profile showing the normalized $CsCd^+/CsTe^+$ value which is calibrated to show the variation in the x-value of the $Hg_{1-x}Cd_xTe$ multilayer structure. The nominal composition is shown in the insert drawing.

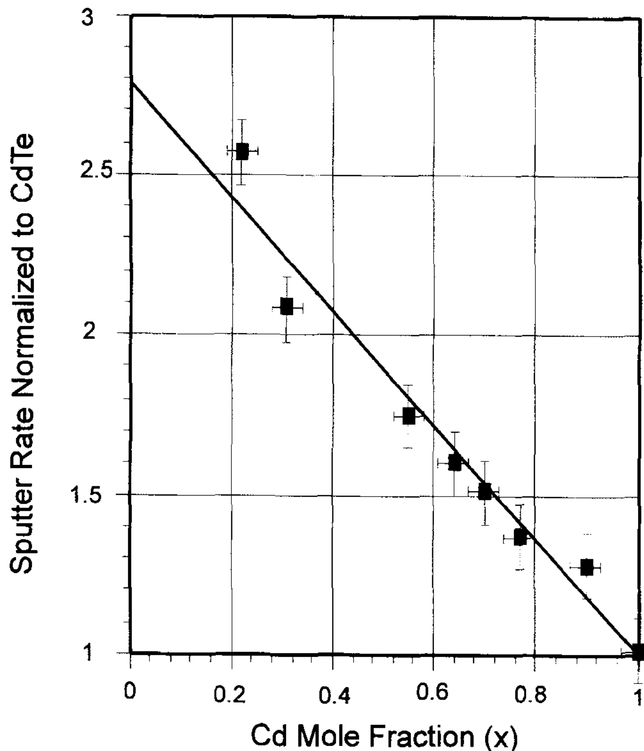

Fig. 5. Plot showing the linear relation between the $Hg_{1-x}Cd_xTe$ composition and the sputter rate for each composition. The data is collected from samples of various sources. Error bars are based upon repeat measurements of samples of each nominal composition. More data is needed to provide better analysis of the relationship between the sputter rate vs $Hg_{1-x}Cd_xTe$ composition.

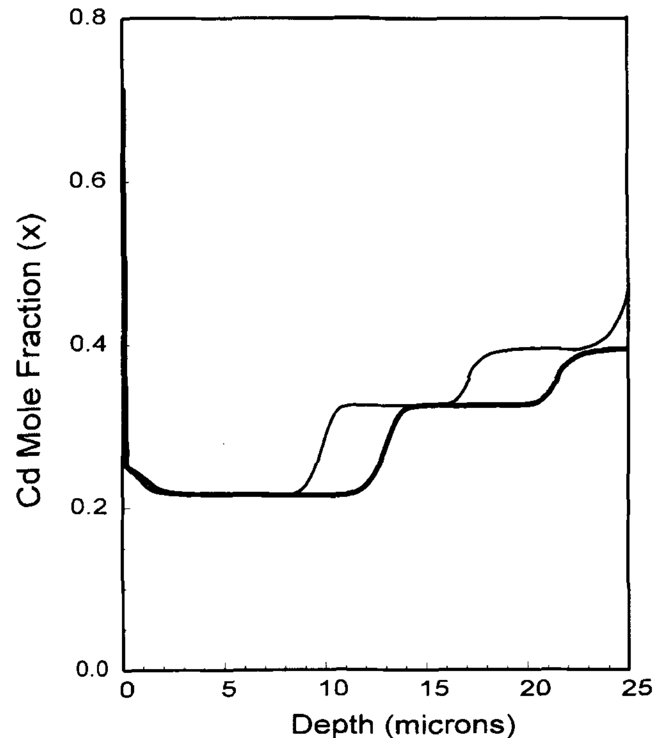

Fig. 6. Multilayer HgCdTe structure, layer thickness plotted using average sputter rate (thin line) and by calibrated sputter rate (thick line). Correction was applied by using the average composition of each layer and the sputter rate for each composition bases on the best fit curve of Fig. 5. The correction is less accurate for the region where there is a slope in the composition profile.

yield with x-value is established by correlating the normalized $CsCd^+$ ion yield with $Hg_{1-x}Cd_xTe$ layers of known composition (Fig. 3). By normalizing the $CsCd^+$ to $CsTe^+$, the changes in the $Hg_{1-x}Cd_xTe$ composition can be accurately determined. Figure 4 shows a SIMS depth profile of a multi-layered HgCdTe sample monitoring the $CsCd^+$ and $CsTe^+$ molecular ions. The advantage of this technique to characterize the HgCdTe composition is that a conversion factor can be established from the normalized $CsCd^+$ ion yield in a CdTe layer or any layer with a known composition. A conversion factor just as any other sensitivity factors used in SIMS analysis can be readily obtained from a known standard. This matrix independent conversion factor can be used to calibrate the x-value for any unknown HgCdTe composition.

Composition Dependent Sputter Rate

The sputtering rate of a SIMS analysis not only depends on the mass, energy, angle of incidence and current density of the bombarding primary ion beam, but also the physical and chemical features of the sample itself (e.g., mass of sample atoms, surface binding energy). Because of the compositional changes in HgCdTe heterostructures, the associated sputter rate for each layer is different. The general procedure for producing a SIMS depth profile is to monitor the secondary ion signal of an element or molecule of interest as a function of sputter time. In a uniform matrix, this can be translated to depth by measuring the sputtered crater by stylus profilometry, the accuracy of the measured depth can be within 2%. In a heterostructure, if the sputter rate variation in different matrix composition is not taken into account, it is in effect assuming the rate at which each layer is removed is the same. Using an average sputter rate in a SIMS depth profile to calibrate the thickness for various layers of HgCdTe heterostructure can give misleading information on the interface depths of the different layers, especially if there is significant difference in the composition of each layer.

We measured a set of HgCdTe single layered samples of different composition ranging from $x = 0.2$ to $x = 1$. Each sample was raster sputtered by Cs primary beam bombardment under identical instrument conditions (same primary current, raster size) to create a square flat bottom crater. These craters are measured by stylus profilometry and the sputter rate for each sample (composition) is determined from the relation of sputtered time vs sputtered depth. It has been found that there is a linear relation between the $Hg_{1-x}Cd_xTe$ composition and the sputter rate for each composition (Fig. 5). This linear relationship enables a simple way to calibrate the thickness of each individual layer in a multilayer HgCdTe structure if the composition of each layer is determined. As shown in Fig. 6, the layer thickness from the uncorrected SIMS depth profile can be off significantly with respect to the actual layer thickness as shown by the

corrected SIMS profile.

SUMMARY

The technique of detecting CsM^+ ions under Cs^+ primary ion bombardment is an improved method for SIMS compositional analysis of II-VI compounds. Quantitation of SIMS data by means of the CsM^+ technique is possible using composition independent relative sensitivity factors. These can be derived from a standard, or directly from a correlation of CsM^+ intensities.

Composition variation of HgCdTe has a strong effect on the sputter removal rate of different composition layers by SIMS. This heterogeneous sputter removal rate has been found to be linearly related to the HgCdTe composition. Calibration of layer thickness in multilayer HgCdTe structure can be performed from the demonstrated linear dependency of the sputter rate with HgCdTe composition.

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