

Quantitative analysis of semiconductor alloy composition during growth by reflection-electron energy loss spectroscopy

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Determination of alloy composition during epitaxial growth of $\text{Ge}_x\text{Si}_{1-x}$ alloys has been demonstrated using reflection-electron energy loss spectroscopy (REELS) at reflection high-energy electron diffraction (RHEED) energies. Measurements of inelastic scattering intensities from Si K (1840 eV) and Ge $L_{2,3}$ (1217 eV) core losses were performed using a conventional RHEED gun together with an electron energy loss spectrometer in a molecular beam epitaxy system. Comparison of *ex situ* composition measurements by Rutherford backscattering and energy dispersive x-ray spectroscopy in a transmission electron microscope indicate excellent agreement with composition determination by REELS, demonstrating the capability of REELS as a quantitative *in situ* analysis technique. Application of REELS to other semiconductors is discussed and initial results for III-V and II-VI semiconductor alloys (GaAs, CdTe, and ZnTe) are also presented.

I. INTRODUCTION

Achievement of increased performance and yield in novel semiconductor structures grown by molecular beam epitaxy (MBE), such as strained quantum-well lasers, heterojunction bipolar transistors, and high electron mobility transistors, will depend strongly on the ability to interpret and use chemical information obtained from the growth surface in real time. The structure and composition of the growth surface are determined by a complex interrelationship of the absolute and relative incident molecular beam fluxes, strain, surface reconstruction, surface steps, defect and impurity densities, and substrate temperature. Despite two decades of effort, many of the basic extrinsic and intrinsic physical and chemical quantities characteristic of growth surfaces remain unknown.

Numerous well-developed surface analytical techniques exist for determination of surface structure and composition (e.g., low energy electron diffraction, high-resolution electron energy loss spectroscopy, Auger spectroscopy, x-ray photoelectron spectroscopy, and scanning tunneling microscopy) but none of these can be used during MBE growth, due to incompatibility with the growth environment. An ideal *in situ* analysis technique would be capable of high data-rate operation over long working distances, could be employed for both rough and smooth growth surface morphologies, and would be compatible with the geometry of conventional MBE growth environments. The most commonly used MBE analytical tool, reflection high-energy electron diffraction (RHEED), can probe surface morphology and crystallographic structure, but it does not give direct information about the chemical nature of the surface. Since RHEED is sensitive to surface roughness, it has been used to indirectly infer growth rate and surface composition at the initiation of growth or following growth interrupts in III-V systems, by monitoring periodic oscillations in specular beam intensity. However, this technique is essentially limited to analysis in the two-dimensional island nucleation growth mode, for surfaces with sub-

monolayer initial smoothness. In many instances it would also be desirable to obtain compositional information for surfaces in the microscopically rough and step flow growth modes. Recently developed *in situ* analysis methods, which provide information about surface chemistry, include those based on measurement of sticking coefficient (reflection mass spectrometry),¹ and surface polarization-related optical reflectivity (reflection difference spectroscopy or more general technique of ellipsometry).^{2,3} Each of these methods have advantages and disadvantages closely related to their physical principles of operation.

The purpose of this article is to demonstrate an *in situ* technique, reflection-electron energy loss spectrometry (REELS) at RHEED energies, which can be used in real time to *directly* probe surface composition (and potentially detailed surface chemistry). We discuss the use of *in situ* REELS for compositional analysis of $\text{Ge}_x\text{Si}_{1-x}$ alloys. These results were compared with *ex situ* techniques of Rutherford backscattering (RBS) and energy dispersive x-ray analysis (EDX) in a transmission electron microscope. In addition, initial data on III-V and II-VI semiconductors are discussed. We have recently demonstrated the use of REELS in the early stages of Ge growth on Si.^{4,5} The advantage of this technique, in addition to the inherent surface sensitivity ($< 20 \text{ \AA}$) and compatibility with different (III-V, IV-IV, and II-VI) semiconductor MBE growth systems, is that its results are complementary to RHEED data and are simultaneously obtained.

RHEED energies range from 10 to 30 keV primary beam energy, and in the work reported here, we have found it advantageous to use as high a primary beam energy as possible because the inelastically scattered electrons of interest (up to 2 keV) are strongly forward scattered,⁵ and thus inelastically scattered electrons are efficiently detected at long working distance. While this range of inelastically scattered electrons limits us to the analysis of K ionizations up to Si (1840 eV), L and M transitions for the elements in other important IV-IV, III-V, and II-VI compounds all fall within this easily detectable range.

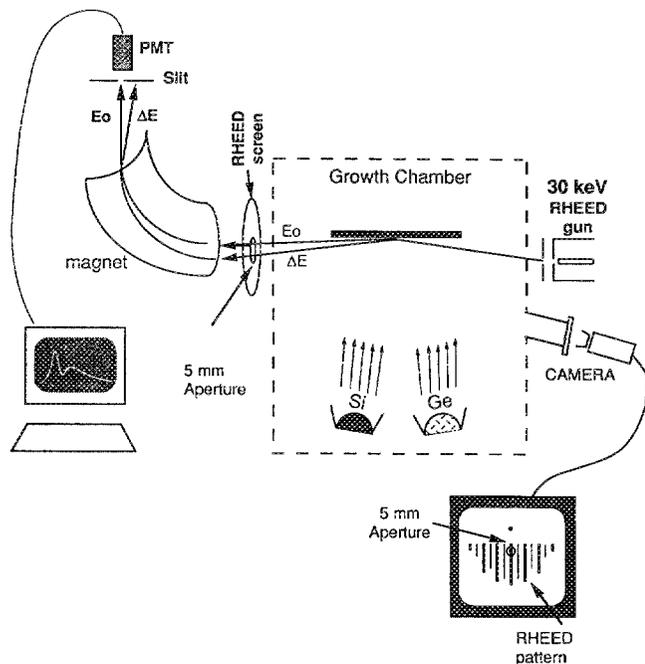


FIG. 1. Schematic of RHEED/REELS system. Electrons within a small angular range pass through the RHEED screen and are dispersed by the 90° sector magnet. The dispersion of elastically and inelastically scattered electrons is ramped across an energy selecting slit and the spectrum is measured by analog or pulse counting electronics. The RHEED pattern is also simultaneously monitored using a video camera and frame grabber.

II. EXPERIMENTAL

We have modified a serial electron energy loss spectrometer typically used on an electron microscope to work with a RHEED-equipped MBE growth chamber and details have been given elsewhere.^{4,5} A schematic of the system is shown in Fig. 1. The REELS scattering geometry employed in the present work is similar to a conventional RHEED configuration, with an electron beam incidence angle of $\phi \approx 37$ mrad. Using a video camera and frame grabber, structural analyses by RHEED at 30 keV with an emission current of 30 μ A and sample current of approximately 1 μ A were performed simultaneously with the REELS measurements. The RHEED screen in our work is a phosphor-coated Al screen. A 5 mm opening at the screen center allows passage of electrons to the energy loss spectrometer. The measured energy resolution of approximately 7 eV for our conventional RHEED gun-equipped system is consistent with electromagnetic lens calculations⁴ and is adequate for quantitative analysis of core losses over continuum transition windows of tens or hundreds of electron volts. The primary limitations of the energy resolution during an actual experiment result from the RHEED gun beam waist, and the long interaction length for a sample analyzed at grazing incidence. Improved energy resolution would require electron optics with a large depth of focus, a feature for which the present system was not designed. Further improvement in energy resolution resulting from the use of a RHEED gun with smaller virtual source and from sampling shorter samples would allow for the study

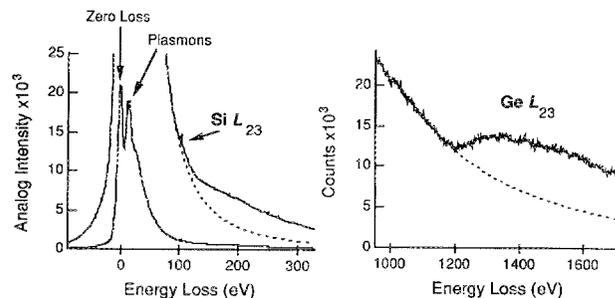


FIG. 2. Typical REELS spectrum from a 2 Å epitaxial layer of Si grown on Ge (001) showing intense zero loss and surface plasmon peaks. Weaker core losses from Si (99 eV) (scaled 12 \times) and Ge (1217 eV) $L_{2,3}$ (scaled 1000 \times) can also be seen above background.

of near-edge structures in core losses, a sensitive tool for understanding the nature of chemical bonding.

A typical REELS spectrum, in this case taken from a 2 Å Si film deposited onto a Ge (001) substrate, is shown in Fig. 2 and comprises a zero loss peak, low loss features (which consist of surface and bulk plasmons) and a Si $L_{2,3}$ edge. At greater energy losses, the contribution from the substrate Ge $L_{2,3}$ core loss (scaled by 1000 \times) can be seen. One of the more surprising aspects of RHEED data, which REELS has revealed, is the substantial fraction of inelastic intensity (typically > 80% of the total intensity) over small angular ranges around Bragg rods.

III. COMPOSITIONAL ANALYSIS DURING Si-Ge ALLOY GROWTH

Epitaxial $\text{Ge}_x\text{Si}_{1-x}$ alloys were grown at 410 °C on Si (001) substrates in a custom-designed MBE system, with intended compositions of $x = 0$ to 0.5 as determined by quartz crystal oscillators in the vicinity of the electron beam Ge and Si sources. All RHEED patterns showed that the Si buffer layers and alloy films were epitaxial, but trans-

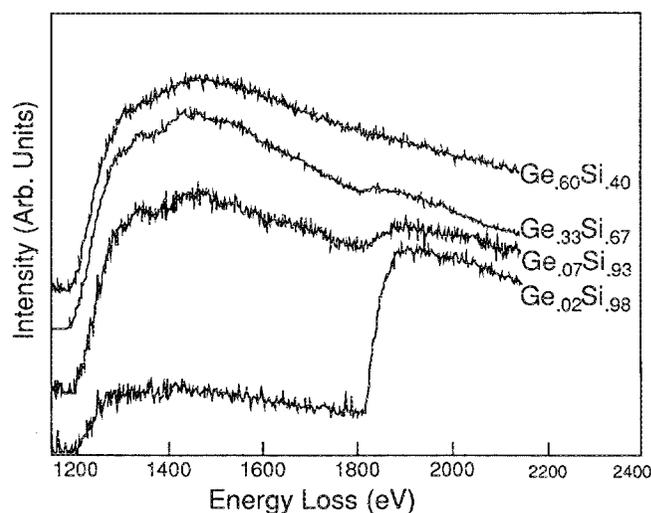


FIG. 3. Background subtracted $L_{2,3}$ and Si K edges $\text{Ge}_x\text{Si}_{1-x}$ alloys grown with intended compositions of $x = 0.05, 0.10, 0.20,$ and 0.50 . Compositions as determined by REELS are indicated in the figure.

TABLE I. Comparison of Ge fraction measured from postgrowth bulk analysis of $\text{Ge}_x\text{Si}_{1-x}$ alloys with *in situ* REELS.

RBS	TEM/EDX	REELS
0.02	0.02	0.02
0.06	0.04	0.07
0.13	0.15	0.21
0.30	0.28	0.33
0.65	0.61	0.60

mission electron microscopy of cross sections indicated stacking faults in some samples.

Si (001) substrates were inserted into the growth chamber and briefly heated to 700 °C to remove the thin layer of native SiO_2 , and a Si buffer layer was grown until a smooth, clean surface as evidenced by the Si (001) 2×1 reconstruction was observed. Film thickness and stoichiometry of alloys were monitored by oscillating quartz crystals (previously calibrated against RBS). Electron energy loss spectra were collected for 40 s after growth completion. Figure 3 shows data from single spectra, which have been background stripped. Note that data presented here are not averaged or differentiated, as is done in Auger analysis, although such an approach may be useful for detection of much lower concentrations. Signal levels are strong enough, even in the case of a dilute alloy, to analyze the raw data. For quantitative REELS analysis, ionization cross sections were calculated for each core-loss edge of interest, and the ratios of calculated cross sections were compared to the ratios of the measured core loss intensity ratios. Because these calculations are made for single atoms, the intensities when integrated over fixed energy windows, represent the relative intensities that one would expect for a stoichiometric $\text{Ge}_{0.5}\text{Si}_{0.5}$ alloy. We can relate the concentration of Ge (C_{Ge}) and Si (C_{Si}) to the intensity of the integrated ionization edges (I_{Ge} and I_{Si} for Ge and Si, respectively) by

$$\frac{C_{\text{Ge}}}{C_{\text{Si}}} = k \frac{I_{\text{Ge}}}{I_{\text{Si}}},$$

where k is a scaling factor.

We can infer from our calculations that because the Ge $L_{2,3}$ cross section is so much larger than the Si K cross section, that this approach should be especially sensitive to low concentrations of Ge. Previous studies, which used theoretical cross sections computed with single scattering transmission data, yielded accuracies on the order of 20% when cross sections are normalized to regions far from the ionization edge.⁶ REELS indicates a $x = 0.026$ composition when a theoretical cross section is used over a 200 eV energy window, while postgrowth analysis using RBS reveals an alloy composition of 0.02 and transmission electron microscopy (TEM)/x-ray microanalysis also indicated $x = 0.02$. There are several possible reasons as to why the REELS value differs by 25% from the postgrowth

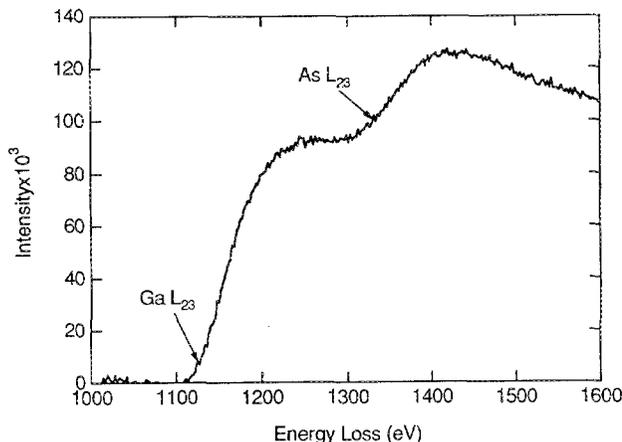


FIG. 4. Ga and As $L_{2,3}$ edges from GaAs.

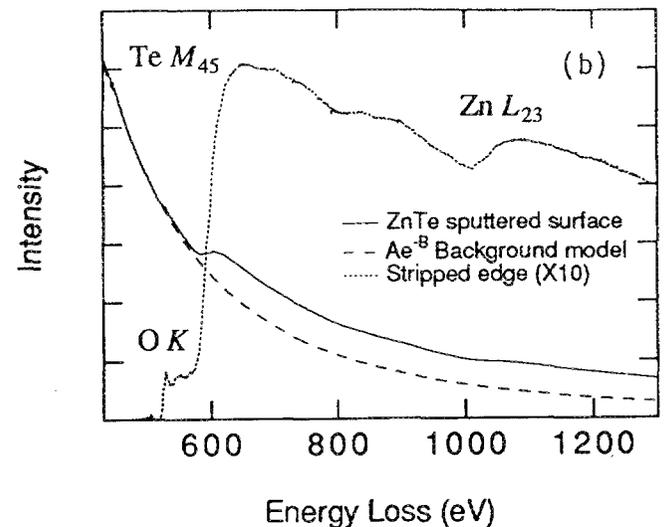
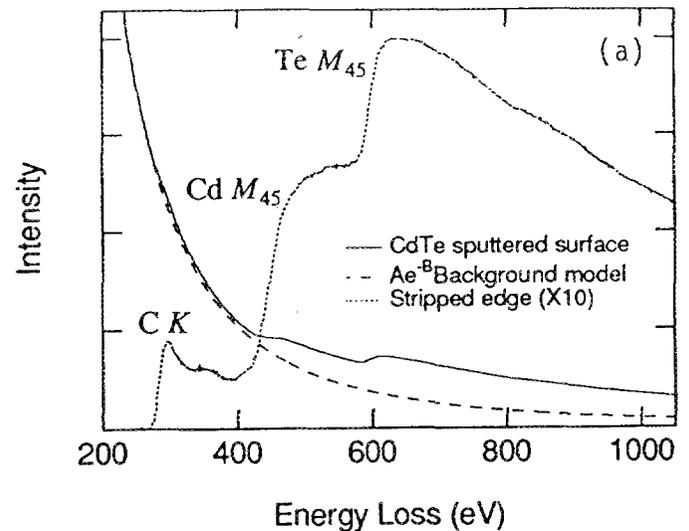


FIG. 5. (a) Cd and Te $M_{4,5}$ edges from a $1 \mu\text{m}$ CdTe film grown onto GaAs. The CdTe film was cleaned by sputtering but surface contamination can be detected as evidenced by the C K edge at 285 eV. (b) Te $M_{4,5}$ and Zn $L_{2,3}$ edges from a $1 \mu\text{m}$ ZnTe film grown onto GaAs (001) surface. Oxygen surface contamination can be detected as evidenced by the O K edge at 532 eV.

analysis values. REELS, under the conditions we have used, is very surface sensitive, and some layer by layer variation of composition may have occurred during growth, something which would not be detected by RBS or TEM/x-ray microanalysis, because the latter average data over the entire volume analyzed. It is also possible that comparison with theoretical cross sections may not be sufficiently accurate and that accurate compositional information can be obtained only by using empirically determined cross sections for a given scattering geometry. For this reason, we have selected the empirical cross sections from the dilute alloy as the correct values, and the other alloy compositions are determined using this cross section. Results of this comparison shown in Table I exhibit excellent agreement with RBS and TEM/x-ray data. Background extrapolation over a 200 eV window may also be a source of error.⁵

IV. RESULTS FOR III-V AND II-VI SEMICONDUCTORS

In order to provide a demonstration of the feasibility of REELS at RHEED energies for III-V and II-VI compounds, GaAs, CdTe, and ZnTe surfaces were also examined. A bulk (001) GaAs crystal, was briefly heated to 650 °C in the absence of growth beams until a clean (001) surface, as revealed by RHEED was visible. These annealing conditions should have resulted in a Ga-terminated surface. As shown in Fig. 4, the Ga and As $L_{2,3}$ edges are clearly apparent and distinguishable, despite the broad ionization edge features.

Films of CdTe and ZnTe 1 μm thick, which were grown by MBE on (001) GaAs, were also examined. Samples were prepared by polishing in a Br-methanol solution followed by sputter etching at 1 keV. The surfaces were examined in reflection mode at 100 keV in a Philips EM430 TEM, equipped with a Gatan parallel energy loss spectrometer and are shown in Figs. 5(a) and 5(b). These data show not only the Cd and Te $M_{4,5}$ and Zn $L_{2,3}$ edges, but also show C and O surface contaminants, which were ei-

ther incompletely removed during surface sputtering or which contaminated the sample surfaces during analysis in the high vacuum environment of the TEM column. Although quantitative interpretation of these results is not possible, it is clear that a number of core loss transitions for these materials are accessible in the 2 keV detection range, as for Ge and Si.

V. CONCLUSIONS

We have demonstrated the use of REELS as a quantitative *in situ* probe of surface composition during MBE and have applied the technique to the study of $\text{Ge}_x\text{Si}_{1-x}$ alloys grown on Si (001). In this *in situ* technique, simultaneous structural and chemical information can be obtained from the surface due to the complementary nature REELS and RHEED. Our initial data on the analysis of GaAs, ZnTe, and CdTe indicate the considerable potential of REELS analysis for characterization of compound semiconductor surfaces during MBE growth.

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¹J. Y. Tsao, T. M. Brennan, and B. E. Hammons, Appl. Phys. Lett. **53**, 288 (1988).

²D. E. Aspnes, J. P. Harbison, A. A. Studna, and L. T. Florez, J. Vac. Sci. Technol. A **6**, 1327 (1988).

³D. E. Aspnes, W. E. Quinn, and S. Gregory, Appl. Phys. Lett. **56**, 2569 (1990).

⁴H. A. Atwater and C. C. Ahn, Appl. Phys. Lett. **58**, 269 (1991).

⁵C. C. Ahn, S. Nikzad, and H. A. Atwater, Mat. Res. Symp. Proc. **208**, 157 (1991).

⁶C. C. Ahn and P. Rez, Ultramicroscopy **17**, 105 (1985).