RAMAN SCATTERING AND X-RAY DIFFRACTION CHARACTERIZATION OF AMORPHOUS SEMICONDUCTOR MULTILAYER INTERFACES

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ABSTRACT

In the present study, Raman spectroscopy (RS) and x-ray diffraction have been used to characterize semiconductor multilayer interfaces. A model for Raman spectra of multilayers is developed and applied to the specific case of the interfaces of a-Si/a-Ge multilayers. Quantification of the "blurring" of interfaces is possible because RS is capable of directly "counting" the total number of chemical bonds of a given type in the film. Multilayers, prepared by various deposition techniques, are compared. Several a-Si/a-Ge multilayers deposited by UHV evaporation (MBD) exhibit exceptionally sharp interfaces (intermixing width <1.0Å) and regular periodicities.

INTRODUCTION

Recent developments in thin film technology have made it possible to prepare and characterize very regular, periodic, multilayered thin film structures. This has created a great deal of interest, both on a basic and on a technological level. Several groups [1,2], have prepared periodic structures composed of alternating layers of tetrahedrally bonded amorphous semiconductors and insulators. In addition, periodic multilayers consisting of alternating thin layers (from 10 to 100Å) of high density and low density materials have been shown to act as efficient Bragg diffractors for x-rays [3,4].

Many prior structural studies sought to establish the existence of regular layering in multilayers and to determine the layer spacing [2,4]. Others sought to observe atom to atom bonding changes which may occur when atoms are constrained in ultrathin films [1,5]. In the present work, we focus on the use of Raman spectroscopy (RS), a novel technique for characterizing semiconductor multilayer interfaces. In particular, a model for the analysis of Raman spectra of semiconductor periodic multilayers [6] is applied to the specific case of a-Si/a-Ge multilayers. Of the films prepared by a spectrum of deposition techniques, including: ultra-high vacuum evaporation (Molecular Beam Deposition, MBD), ion beam (IB) and magnetron sputtering (MS) and glow discharge (GD), MBD multilayers exhibited the sharpest interfaces. The role of substrate temperature, T_s, during deposition is also addressed.

The interfacial roughness parameter determined by low angle x-ray diffraction (LAXRD), is in good agreement with Raman.

EXPERIMENTAL

Amorphous multilayer structures were prepared by a number of techniques. With the exception of those prepared by RF glow discharge process, all films were silicon-germanium multilayers. Periodicities ranging from 22 to 400Å were prepared. The thickness of the silicon and germanium layers in each period were nominally equal.

A PHI-400 MBE system was used for the preparation of the MBD multilayers. Regular layering was achieved using pneumatic shutters in front of the source which were controlled by a thickness monitor. The ion

beam sputtered multilayers were prepared using a 2.5 cm Kaufman ion source operated with Ar. The targets were mounted on a disk on a pivot which could be rotated into the ion beam path for reproducible layering. The ion beam was shut off while the targets are rotating. The magnetron sputtered multilayers were produced by rotating the carousel of a Sloan (SL-1800) horizontal sputtering system. Glow discharge layers of a-SiN_x:H/a-Si:H were grown following the method described in Ref. 7.

In the Raman measurements, the 5145Å line of an Ar^+ ion laser was employed. The LAXRD measurements were obtained using a Phillips XRD-2500 diffractometer equipped for Cr and Cu Kα radiation. From LAXRD, the presence of regular periodicities and interfacial roughness are immediately accessible.

RESULTS AND DISCUSSION

Raman spectroscopy has been shown to be a very useful technique to characterize the structure of single layers of amorphous semiconductors, particularly for a-Si and a-Ge [8]. In Fig. 1a, a typical Raman spectrum for an a-Si (dotted) and an a-Ge (dashed) film is shown. The continuous line represents the sum of the two spectra. For both, a-Si and a-Ge, the Raman spectrum shows two prominent humps located at 140 and 480 cm^{-1} for the former and at 75 and 270 cm^{-1} for the latter. The lower frequency peak has its origin in the transverse acoustic (TA) phonons while the higher frequency one is related to the transverse optical (TO) phonons [8]. Similar to the pure elements, the Raman spectra of a-Si_xGe_{1-x} alloys have been extensively studied [9].

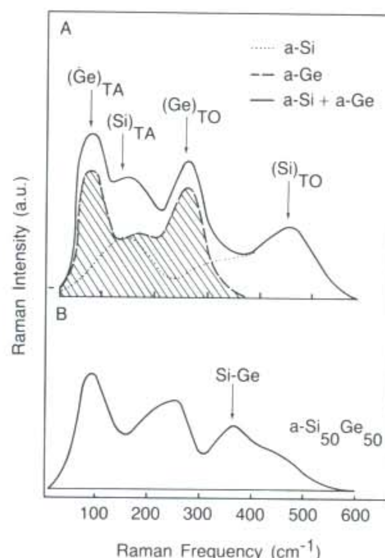

Fig. 1. Typical Raman spectra for an a-Ge, a-Si (dotted) film and the sum of both (continuous). The origin of the Raman peaks are noted above the curves.

Figure 1b shows a typical Raman spectrum for an a-$Si_{.5}Ge_{.5}$ alloy. The spectrum exhibits features common to both a-Si and a-Ge which arise from the vibrations associated with Si-Si and Ge-Ge bond pairs respectively. In addition, a peak that is not present in either the pure a-Si or a-Ge is observed at approximately 380 cm^{-1}. The position of that peak shifts as composition changes. Its relative strength is also a measure of the chemical composition in the alloy and is proportional to x(1-x) for a-$Si_{1-x}Ge_x$.

Previous publication of the uses of RS to characterize multilayered structures focused on its sensitivity to observed quantitative changes in the microscopic structural order of thin layers, particularly the bond-angle distribution width [5]. For the present work, a method that

employs RS data to quantitatively determine the intermixing at interfaces in multilayer structures has been developed [6]. Quantification of the "blurring" of interfaces is possible because peak heights in the Raman spectra are proportional to the number of scatterers, thus RS is able to directly "count" the total number of chemical bonds.

In a periodic multilayer structure having Z layers per period (ABC....Z) the total Raman scattered intensity from the sum of all "X" layers in the structure has been derived [6] and is given by:

$$I_X = \frac{I_o \Sigma_X}{2\alpha_X} \frac{\exp[-2(\alpha_A \ell_A + \ldots \alpha_{X-1} \ell_{X-1})][1-\exp(-2\alpha_X \ell_X)]}{1-\exp[-2(\alpha_A \ell_A + \ldots \alpha_Z \ell_Z)]} \tag{1}$$

where α_X and ℓ_X are the absorption coefficient and the path length of light respectively, in layer "X". The Raman cross section Σ_X has been determined from standard samples following the method described in Ref. 10.

To demonstrate the use of RS to investigate the structure of interfaces in layered films, the model is applied to the specific case of a-Si/a-Ge multilayers. In all the a-Si/a-Ge samples studied, the last layer deposited was silicon. Thus, in Eq. 1, the layers A and C stand for a-Si and a-Ge and B is the interfacial layer which lies between all of the A and C layers and which, according to our Raman measurements, has a composition close to a-$Si_{.5}Ge_{.5}$.

From Eq. 1, the interfacial layer thickness, l_B, can be expressed as:

$$l_B = \frac{[\exp(2\alpha_A \ell_A)-1]}{2[1+\exp(-2\alpha_C \ell_C)]\alpha_A} \Gamma_{AB} \frac{I_B}{I_A} \tag{2}$$

where we have assumed $\alpha_B \ell_B << \ell_A \alpha_A$, $\Gamma_{AB}=\Sigma_A/\Sigma_B$ and $l_B=\ell_B$.

In Fig. 2, the Raman spectra for three a-Si/a-Ge multilayers prepared by MBD (T_s=300C), ion beam (T_s=275C) and magnetron sputtering (T_s=25 C) are compared. Each spectrum has been decomposed in three components; a-Si (dashed line), a-Ge (dotted line) and a-$Si_{.5}Ge_{.5}$ (continuous line) which added together gives the best fit to the measured integrated Raman

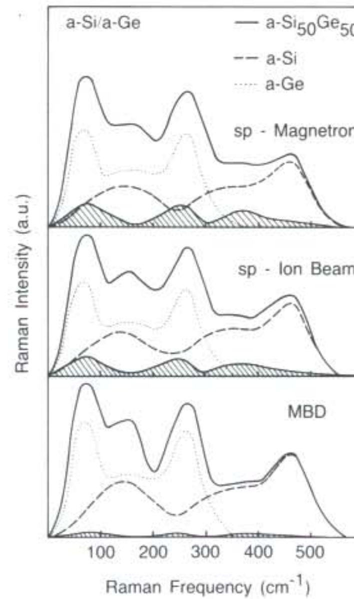

Fig. 2. Raman spectra for a-Si/a-Ge multilayers prepared by magnetron sputtering (top), ion beam sputtering (middle) and MBD (bottom). Each spectrum has been decomposed into three components, a-Si (dashed), a-Ge (dotted), and a-Si_xGe_{1-x}. In all cases, X=0.5.

intensity. Notice that a much reduced a-$Si_{.5}Ge_{.5}$ component is observed for the MBD-sample.

Using Eq. 2, the interfacial layer thickness, l_B, has been determined from the integrated Raman intensities under the a-$Si_{.5}Ge_{.5}$ and a-Si curves. We find that l_B is 3.1Å, 5.3Å and 6.2Å for the MBD, ion beam and magnetron sputtering samples respectively.

Table I. Properties of various Semiconductor Multilayers (Thicknesses in Angstroms)

Composition	Structure[1]	Technique (see text)	T_s °C	LAXRD[3]				Raman
				p	ξ	η	m	w
a-Si/a-Ge	25 (50/50)	MBD	25					0.8
a-Si/a-Ge	50 (10/10)	MBD	300	22				0.2
	25 (75/75)	MBD	300	154	4	.54	14	1.0
	25 (100/100)	MBD	300					<0.5
a-Si/a-Ge	25 (50/50)	IBS	275	104	7.8	.53	9	3.0
a-Si/a-Ge	100 (50/50)	MS	25	111	peak splitting		11	4.0
a-SiN_x:H/ a-Si:H	100 (20/20)	GD	250	54	5	0.6	4	not susceptible to analysis

[1] Number of periods (thickness of a-Si/thickness of a-Ge or SiN_x)

[2] LAXRD data is p (periodicity), ξ (roughness), η (d_{Si}/p or d_{SiNx}/p), m (number of LAXRD peaks observed)

[3] Intermixing width, $w = l_B - 2.2$

l_B contains two components: the number of bonds that an atomically smooth surface would have with the layer above it and any arising from intermixing. The model used to analyze the Raman [6] spectra is microscopic, and mathematically combines these bonds together. l_B is thus larger than the true intermixed layer thickness. To properly calculate intermixing requires a proper accounting of the density of bonds on a growing a-Si or a-Ge film. This quantity can be estimated, based on the fact that for the growth of polycrystalline tetrahedral semiconductors on an amorphous substrate, at the lowest temperature where partial crystallization begins, the (110) and (111) orientations are approximately equal and dominate [11]. The bond density for the (111) and (110) surfaces of $Si_{.5}Ge_{.5}$ are calculated to be 11.3 and $9.2\times10^{14}cm^{-2}$ [12]. The bond density of the amorphous structure just below this temperature might be expected to be similar to the average of the (111) and (110) surfaces, about $10.3\times10^{14}cm^{-2}$. This is equivalent to 2.2Å of $Si_{.5}Ge_{.5}$. The intermixing width, w, for the samples is then 1.0, 3., and 4Å, respectively for the MBD, ion-beam, and magnetron sputtered samples. These numbers are summarized in Table I.

From the LAXRD date, values of the interfacial roughness (ξ) and the thickness ratio of the top layer to the period of the multilayer (η) were calculated using the technique developed by Underwood [4]. Table I contains the periodicity (p) from LAXRD, (ξ), (η), the number of diffraction orders observed (m), and the intermixing width from Raman. The third, fifth and sixth entries in Table I correspond to the samples of Fig. 2.

The MBD samples exhibit the most diffraction orders (14), evidence of exceptional smoothness. We note that interfacial width from Raman is always less than ξ. ξ contains a component from roughness and from intermixing whereas Raman is an inherently interfacially sensitive technique for a-Si/a-Ge multilayers.

Having demonstrated the RS-interface technique, we applied it to study the influence of growth parameters on the interfacial sharpness in MBD-samples. The first set of curves in Fig. 3 shows the Raman spectrum of a series of a-Si/a-Ge multilayers prepared at a fixed T_s=300°C. The period p, has been varied from 22 to 400Å and the nominal thickness of the individual layers was p/2 for all cases. Broad Raman features characteristic of a-Si and a-Ge (Fig. 1) are observed in all multilayers with the exception of the one with p=400Å. In the latter case, in addition to the amorphous component, mainly silicon, there are two sharp lines located at approximately 300 and 520cm^{-1}. These indicate a totally microcrystalline germanium layer and a partially crystallized silicon layer respectively. Notice that no significant interfacial mixing has occurred as indicated by the absence of the Si-Ge peak in the range of 380cm^{-1}. Samples prepared at 25°C were also analyzed in general the lower deposition temperature results in a stronger Si-Ge peak indicating a thicker interfacial layer (see Table I).

Several entries in Table I are conspicuously missing. These point to measurement difficulties characteristic of each technique. RS does not lend itself to studying samples like GD a-SiN_x:H/a-Si:H due to the absence of unique bonds at the interface possessing a higher

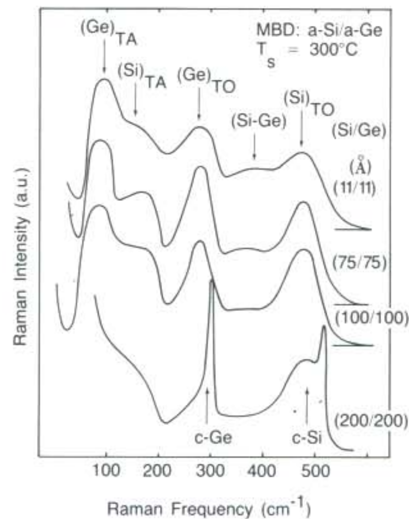

Fig. 3. Raman spectra for four Si/Ge multilayers prepared by MBD. Nominal thickness for the Si and Ge layers are noted in a column on the left. All samples were prepared at T_s=300°C. The position of the Raman line for crystalline Si and Ge are indicated in the bottom of the figure.

cross-section. On the other hand, LAXRD is curtailed if the sample is not sufficiently uniform and regular as in the case for the MS sample. RS does not have this limitation.

CONCLUSIONS

We have employed Raman scattering to investigate the structure of the interfaces in periodic multilayered films. The Raman spectra has been analyzed using a model that allows us to distinguish atomically smooth interfaces from those where interfacial mixing has occurred. The model applied to a-Si/a-Ge multilayers revealed atomically smooth interfaces for multilayers prepared by UHV-evaporation (MBD), whereas samples prepared by other means exhibit slightly wider interfaces. Our Raman results are in good agreement with low angle x-ray analysis in the same samples.

ACKNOWLEDGMENTS

We acknowledge very helpful discussions with Dr. R. Tsu and Prof. F.H. Pollak. We would finally like to thank E.M. Norman and M. Lipton for their tenacious assistance in preparing the manuscript.

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