Non-destructive depth profile analysis for surface and buried interface of Ge thin film on Si substrate by high-energy synchrotron radiation X-ray photoelectron spectroscopy

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Abstract. Non-destructive depth profile analysis with better depth resolution is required for the characterization of nano-materials and their fabrication. X-ray photoelectron spectroscopy (XPS) is the typically non-destructive analysis, however, XPS with fixed excitation energy source cannot provide depth profile without additional technique, such as ion beam sputtering. On the other hand, analyzing depth of XPS can be varied with the energy tunable excitation source, such as the synchrotron-radiation (SR), since the escape depth of the photoelectrons depends on their kinetic energy. We can obtain the XPS spectra from different analyzing depth by varying excitation energy. This technique can provide depth profile non-destructively. In the present study, Ge thin films on Si substrate has been analyzed to obtain depth profile of the thin film and buried interface of Ge/Si under the film.

1. Introduction

The depth profile is one of the most essential information for the characterization of material surfaces. Recent progress of "nano-technology" requires the high quality depth profiling in nm range. In order to obtain precise results of depth profile, there are several important factors, such as resolution (lateral and depth), sensitivity, destructivity, etc. Sputter etching is commonly used for the conventional way of depth profiling. However, it makes damage of the analyzing area because of atomic mixing and surface roughening. If the depth profile analysis is performed non-destructively, the analysis is greatly improved. The XPS (X-ray Photoelectron Spectroscopy) is one of the typical non-destructive analyzing methods. However, it cannot provide depth profile without additional techniques, such as sputtering, since conventional XPS has the fixed analyzing depth.

A possible method of non-destructive depth profile analysis is the use of synchrotron-radiation (SR) which is a high-energy and continuously variable-energy excitation source, in order to observe the dependence of the signal intensity on the kinetic energy of photoelectrons. The escape depth of photoelectron depends on their kinetic energy. Tanuma et al. have shown [1] the precise results of the inelastic mean free path (IMFP), which is directly related to the escape depth, as a function of the kinetic energy of electrons. On the basis of their results, we can vary the escape depth in XPS by varying X-ray energy. It is therefore possible that the depth profile is obtained non-destructively by...
measuring spectra under the various X-ray energies. In the present study, a "High-energy SR-XPS" has been applied to the depth profile analysis for surface and buried interface of Ge thin film on Si substrate.

2. Experimental
The high-energy SR-XPS (1800~3700 eV) measurement has been performed at Beam Line 27A at the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF) [2]. The radiation was monochromatized by a double crystal monochromator using the InSb(111) plane. The energy resolution of this beam line was 0.9 and 1.5 eV at the photon energy of 2000 eV. The photon flux was 3.8 x 10^{11} photons·s^{-1}·cm^{-2} at 2100 eV. The incident X-ray was irradiated at an angle of 55° from the surface normal and the take-off angle of the photoelectron was 90°. The electron spectra were obtained using a hemispherical electron energy analyzer. The analyzer was operated under the fixed analyzing energy mode with a pass energy of 10 eV, which yielded a full width at half maximum (FWHM) of 1.2 eV for the Au 4f_{7/2} line at the photon energy of 2100 eV. The kinetic energies of the photoelectrons were calibrated such that the binding energy of the Au 4f_{7/2} line of metallic gold is \( E_b = 84.0 \) eV using an MgKα and SR X-ray. Measurements of the samples were performed under a pressure of 3 x 10^{-8} Pa.

The samples used were vacuum vapor deposited Ge with 2 nm (sample #1,#2) and 4 nm (#3,#4) thickness on the Si(100) single crystal, respectively. The thickness was monitored by quartz crystal oscillator. The Si substrate surfaces were treated as two different ways. One of the substrate was chemically treated and subsequently terminated with hydrogen (sample #1,#3). Another one is just supersonically rinsed with acetone and has native oxide layer (#2,#4).

3. Results and Discussion

1. Ge overlayer analysis
Figure 1 shows the X-ray energy dependence of the typical Si 1s (\( E_b = 1839 \) eV) and Ge 2p (\( E_b = 1217 \) eV) XPS spectra for the 2nm Ge deposited on Si(100) substrate which has native oxide layer (sample #2). The spectra were obtained in the X-ray energy range between 1800 and 3700 eV. In the Si 1s spectra, Si and Si^{4+}(SiO_{2}) peaks can be observed in each spectrum, respectively. Suboxide peaks, which are appeared in the intermediate energy of Si and Si^{4+}, are also clearly shown in the spectra taken at 2100 eV. Such suboxide peaks are scarcely observed at the higher excitation energy of X-ray. The intensity of elemental Si becomes dominant with increase of the X-ray energy, in contrast with that of oxides.

In a number of recent works, reliable results of calculation, which is related to the IMFP, attenuation length (AL), escape depth (ED) are shown by Tanuma et al. [1], Penn et al. [3], Jablonski et al. [4] and

![Figure 1](image-url)
other researchers [5]. In these works, Tanuma et al. have shown precisely calculated results of IMFP for various elements and compounds as TPP-2M [1]. In the case of elemental Si, the IMFP is 0.78 and 4.25 nm at \( E_k = 200 \) and 2000 eV, respectively. If this relationship can be extrapolated, the IMFP reaches 10 nm at \( E_k = 4000 \) eV. These data strongly suggest that deeper surface region can be observed by using higher energy X-ray. These values are used for the depth profile analysis in the present experiments.

In order to interpret these XPS spectra into depth profile, following method, which has been used for the analysis by the take off angle measurements [6], can be applicable for the SR-XPS measurements. If the maximum escape depth of the sample is divided into equal and parallel \( N \) layers, which have thickness \( d \), the current of photoelectrons excited from GeO\(_2\) in the \textit{n}th layer, \( i_n(\text{GeO}_2) \), can be described as follows, since the take off angle of the photoelectrons, \( \theta \) was 90°,

\[
i_n(\text{GeO}_2) = K \sigma \varepsilon_n(\text{GeO}_2) \times \left[ 1 - \left( c_n(\text{GeO}_2) \exp \left( -\frac{d}{\lambda(\text{GeO}_2)} \right) \right) + \left( 1 - c_n(\text{GeO}_2) \right) \exp \left( -\frac{d}{\lambda(\text{others})} \right) \right]
\]

where \( K \) the instrumental function, \( \sigma \) the photoionization cross-section [7], \( \lambda \), the IMFP in oxide, is defined as the distance for which \( 1/e \) of the electrons have not been inelastically scattered, \( c_n(\text{GeO}_2) \) the concentration of GeO\(_2\) in the \textit{n}th layer \((0 \leq c_n \leq 1\), concentration of other components: \(1-c_n\)). The detected intensity of GeO\(_2\) from the \textit{n}th layer, \( I_n(\text{GeO}_2) \), is attenuated in the upper \((1-n-1)\) layers. The \( I_n(\text{GeO}_2) \) can be therefore described by eq. (2).

\[
I_n(\text{GeO}_2) = i_n(\text{GeO}_2) \times \prod_{n=1}^{N-1} c_n(\text{GeO}_2) \exp \left( -\frac{d}{\lambda(\text{GeO}_2)} \right) + \left( 1 - c_n(\text{GeO}_2) \right) \exp \left( -\frac{d}{\lambda(\text{others})} \right)
\]

The intensity of Ge, \( I_n(\text{Ge}) \), can be described with the same way. The observed intensity ratios, \( \frac{I(\text{Ge})}{I_n(\text{GeO}_2)} \) is described by eq. (3).

\[
\sum_{n=1}^{N} I_n(\text{Ge}) / \sum_{n=1}^{N} I_n(\text{GeO}_2)
\]

According to eq. (3), the experimental values of both samples (#1, #2) are almost constant with the kinetic energy of photoelectron. This tendency is same as the calculated values. The experimental ratios are similar with the calculated value of 0.9-1.1 nm (GeO\(_2\)-Ge). This result shows that the oxide thicknesses of both #1, #2 samples are around 0.9 nm. The same process can be also applied for the samples #3, #4. The thickness of GeO\(_2\)-Ge for both samples is 1.6-2.4 nm, respectively.

2. Buried interface analysis

The high-energy XPS is next applied to the analysis of the buried interface by using the samples which have 2 and 4 nm Ge overlayer, which shows the ability of the deeper surface analysis. Figure 2 shows the calculated (broken lines) and experimental (marks) \( I(\text{Si}) / I(\text{SiO}_2) \) ratios as a function of photoelectron kinetic energy. For the SiO\(_2\) film thickness measurements, calculation of \( I(\text{Si}) / I(\text{SiO}_2) \)
I(SiO₂) ratios can be more simplified compared with the eqs. (1)-(3).

If the interface Si oxide layer has the thin uniform structure, the peak intensity from the Si oxide film (I(SiO₂)) of thickness d is given by eq. (4) [8].

\[ I(SiO₂) = K \sigma \int_0^d \exp \left( \frac{-x}{\lambda(SiO₂)} \right) dx = K \sigma \lambda(SiO₂) \left( 1 - \exp \left( \frac{-d}{\lambda(SiO₂)} \right) \right) \]  

(4)

On the other hand, the intensity from the substrate (I(Si)) can be described by eq. (5).

\[ I(Si) = K \sigma \int \exp \left( \frac{-d}{\lambda(Si)} \right) \exp \left( \frac{-(x-d)}{\lambda(Si)} \right) dx = K \sigma \lambda(Si) \exp \left( \frac{-d}{\lambda(Si)} \right) \]  

(5)

The intensity ratio between substrate (I(SiO₂)) and oxide (I(Si)) can be shown from eqs. (4) and (5), as follows.

\[ \frac{I(Si)}{I(SiO₂)} = \frac{\lambda(Si) \exp(-d/\lambda(SiO₂))}{\lambda(SiO₂) \left( 1 - \exp(-d/\lambda(SiO₂)) \right)} \]  

(6)

According to eq. (6), thickness d of the oxide layer on the substrate can be estimated by the relationship between the intensity ratio I(Si) / I(SiO₂) and \( \lambda \) which is a function of kinetic energy of photoelectrons. On the basis of the curve fitting for the observed data with the calculated curve, the oxide thickness is estimated as 0.7 nm for the naturally oxidized Si samples (#2, #4). The oxide layer at the interface of the sample #1 can be estimated as 0.2 nm, which corresponds to almost one atomic layer. The substrate surface of #1 was chemically etched. It is considered that the substrate surface has been slightly oxidized after the etching or during film formation. The results of the sample #3 show different tendency from the calculated curve, since the oxide layer is no more regard as uniform film. The chemical shift of the Si 1s spectra of #3 shows the film is formed by suboxides.

4. Conclusion
On the basis of the results of present experiments, it is demonstrated that the "High-energy SR-XPS" can provide information from surface and buried interface in nm range non-destructively. In order to obtain more accurate profile, several parameters should going to be revised by using effective attenuation length data provided from NIST (National Institute of Standards and Technology) [9], which will be extended from the 50~2000 eV to more higher energy of electrons. It is expected that this analyzing method prov can provide more accurate depth profile in addition to the conventional depth profiling method.

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