X-ray Photoelectron Spectroscopy study of germanium oxidation

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Abstract

The growth of thin layer of oxide on semiconductor substrate is a step of crucial importance in the fabrication process of solid-state devices. In this work, we have used x-ray Photoelectron Spectroscopy (XPS) to investigate the growth kinetics of oxide layers on germanium single crystals under various experimental conditions. In-situ oxidation experiments were carried out in a heating cell attached to the electron spectrometer. The analysis of XPS spectra suggests the growth of non-uniform oxide layer. A model is suggested to define an apparent thickness of the oxide layer as a function of the actual thickness of the oxide islands and the fraction of the oxidized surface. Angle resolved XPS measurements strongly support our model.

1. Introduction

Studying thin layers on top of substrate is an important subject in oxidation/ corrosion chemical vapor deposition studies. The X-ray Photoelectron Spectroscopy (XPS) surface sensitive technique of choice for ultra-thin films (< 30 Angstroms). XPS is basically elemental and chemical information about the top layer of the surface. XPS is in exciting a surface with x-rays of specified photon energy to excite the inner shell of atoms. For the excited photoelectrons to emerge and be detected they must be coming within the top monolayers not deeper than few mean free paths or attenuation length what makes XPS a surface sensitive technique. The photoelectrons intensity versus atomic binding energy gives finger print identification of the atoms. The energy of level is sensitive to the atomic environment, which gives the possibility to study the state of various elements. For a certain XPS line, the peaks that originate from the same atoms are distinguishable from the one from the oxide film. The quantitative analysis is to fit the experimental XPS peaks and to calculate their area after proper back subtraction. The quantitative analysis of the XPS lines can be used to measure thickness of thin overlayers. The method is based on the attenuation of the photo signals emitted from the substrate and from the layer. It has been used by many authors to characterize the thickness of oxides grown on various substrates including silicon and carbide. [1-2]. We present in this paper a critical description of the technique and sh its limits along with its application to the study of germanium oxide layers grown by oxidation.
2. Thickness Estimation by XPS

In the following section we give a brief description of the method along with the equations that are used. We present first the simple case of a uniform layer that is common in the literature. Then we present a modified method that can be used to a non-uniform layer.

2.1 Uniform Thickness Model

Let us consider a uniform layer of certain material residing on top of a substrate. The layer could be an oxide of the substrate or an externally applied layer and in both cases its signal can be differentiated from the substrate's signal. The x-rays excite photoelectrons of both the substrate and the layer; see Figure 1.

![Figure 1: Uniform thickness estimation](image)

The contribution $dl$ of the slab $dx$ to the emerging signal is given by:

$$dl = I'(x) \exp(-x/\lambda)dx$$

(1)

Where $I'(x)$ is the signal originating from depth $x$, $\exp(-x/\lambda)$ is the exponential decay due to the partial loss of photoelectrons before emerging from the surface, $\lambda$ is the attenuation length or the inelastic mean free path (IMFP). For simplicity, let us consider the case of an oxide layer MO covering the surface of the metal M. Equation (1) can be integrated to evaluate the signals $I_{M,\text{sub}}^o$ and $I_{M,\text{ox}}^\infty$ coming from both the substrate and the layer respectively:

$$I_{M,\text{sub}}^o = I_0^o e^{-\delta/\lambda}$$

(2)

$$I_{M,\text{ox}}^\infty = I_\infty^o (1 - e^{-\delta/\lambda})$$

(3)

Where $I_0^o$ and $I_\infty^o$ refer to the signals from a bare surface of the substrate and from an infinitely thick layer of oxide (compared to $\lambda$). Equations 2 and 3 can be solved for $\delta$:

$$\delta = \lambda \ln \left[ \frac{I_{M,\text{ox}}^\infty}{I_{M,\text{sub}}^o} \frac{I_0^o}{I_\infty^o} + 1 \right]$$

(4)

The value of the attenuation length $\lambda$ can be calculated for different materials using the expression given by Seah and Dench [3]. The ratio $I_0^o/I_\infty^o$ can be obtained experimentally combining Equations 2 and 3: $I_{M,\text{ox}}^\infty = I_\infty^o - (I_0^o/I_\infty^o) I_{M,\text{sub}}^o$.

Furthermore, it is possible to use two XPS lines of the metal M of different energies (say A and B with IMFP $\lambda_A$ and $\lambda_B$ to estimate the thickness. The substrate signal $I_{M,\text{sub}}^o$ of Equation 2 can be rewritten for A and B to give:
\[
\delta_{A,B} = \frac{\lambda_A}{1 + \frac{\lambda_A}{\lambda_B}} \ln \left[ \frac{I_{M,A}^{\subscript{NM}}}{I_{M,B}^{\subscript{NM}}} \left( \frac{I_B^0}{I_A^0} + 1 \right) \right]
\]  

This method requires the knowledge of the \(I_A^0/I_B^0\) ratio, which can be obtained from surface of the sample (e.g. by heating or ion bombardment of the substrate).

2.2 Islands Model

The above procedure assumes that the top layer is uniform. However, this condition be met in many practical cases [4]. For instance, let us assume that the layer is composed some islands with an average thickness \(\delta\) covering part of the surface. The bare regions constitute a fraction \(\theta\) of the total surface as illustrated in Figure 2. Equations 4 and 5 can be re-expressed as follows:

\[
I_M^{\subscript{NM}} = \theta I_A^0 + (1-\theta) I_B^0 e^{-\delta/\lambda}
\]  

\[
I_M^{\subscript{NM}} = (1-\theta) I_A^0 + \theta e^{-\delta/\lambda}
\]  

For an assumed fixed value of the exposed fraction \(\theta\), we define the thickness obtained using Equation 4 as the “apparent thickness”. Using Equations 6 and 7, one obtains:

\[
\delta_{\text{apparent}} = \lambda \ln \left[ \frac{(1-\theta) e^{\delta/\lambda}}{\theta + (1-\theta) e^{-\delta/\lambda}} \right]
\]  

In case of thick layers, the exponential factor in the above equation vanishes as \(\delta \gg\) result, the apparent thickness saturates at constant value of \(\lambda \theta \). The actual thickness be obtained after finding \(\theta\) by re-arranging Eq. 8 as follows:

\[
\delta = \lambda \ln \left[ \frac{(1-\theta)}{\exp(-\delta_{\text{apparent}}/\lambda) - \theta} \right]
\]  

In the next section we use the above methods to estimate the thickness of oxide obtained by thermal oxidation of germanium substrates.

![Figure 2: Layer of islands model](image)

3 Germanium Oxidation

The oxidation of germanium substrates was investigated at 380°C under 1 atm press ambient air. Ge2p and Ge3d XPS lines were systematically collected after successi treatments of various durations. The experimental details are given elsewhere [5]. Ti spectra were obtained using an aluminum anode of 1486.6eV Kα x-ray line. The : regions including the Ge2p3/2 (binding energy Eb=1217eV), Ge3d (29.6eV), an (532eV) lines were scanned with 0.05 eV step size after each heat treatment. T (Eb=284.5eV) carbon line was scanned and used as a reference to perform the char correction.

3.1 Data Analysis
Figure 3 shows the time evolution of Ge2p3/2 and Ge3d lines respectively under treatments for the indicated accumulated oxidation treatment time. The 1217 eV energy peak is related to the substrate germanium (Ge0), while the energies of the possible oxidation states of germanium oxide top layer (Geox) reside in the region 1220 eV. The Ge3d region has a main peak at 29.4 eV of elemental Ge beside a broad peak spanning the 31-34 eV range related to the oxidized Ge states. The signal for the oxidized germanium (Geox) clearly increases with the treatment time.

![Figure 3: The progress of Ge2p3/2 (a) and Ge3d (b) peak intensity distribution under oxidation](image)

The signal intensities are taken as the area under the peaks and are computed using the experimental spectra. The fitting parameters include the position, the width of the peaks in addition to the Gaussian/ Lorentzian mixing coefficient. The resolution XPS study of oxidized germanium surface performed by Shmeisser et al. gives binding energies of the four possible oxidation states Ge0, Ge2+, Ge3+, Ge4+. The binding energy of the oxidized states are shifted from the non-oxidized state by 0.80, 1.8, 2.6, and 3.4 eV higher side [6]. The energy resolution of our electron spectrometer (1.4 eV) was used to resolve the different oxidized states. Consequently, we fitted the broad oxidized peak into four peaks. For the thickness calculation, we considered the sum of the intensities of fitting peaks (i.e. $I_{3d_{\alpha=1-4}^{ox}}$) as an effective oxidized signal $I_{Ge^{ox}}$.

The assumption that we have four oxidation states is not a mere reliance on literature as we have evidence that oxidation states exist. Figure 4(a) indicates that the maximum of the oxidized peak shifts towards higher BE. This observation can be explained by the fact that the fourth oxidation state is increasing relative to the other states and shifts the maximum. If only two peaks are used to fit the experimental spectra, one would find that the width of the oxidized peak is about 30% higher than that obtained from germanium dioxide powder in the early oxidation stage. Subsequently, the width decreases and becomes closer to the GeO2 value (see Figure 4(b)). This suggests the increase of the proportion of the higher oxidation states at the expense of the lower oxidation states.

The areas under the peaks of the germanium substrate and germanium oxide lines were computed and tabulated versus the accumulated oxidation treatment time. The next step is to compute the oxide layer thickness progress using the above models.
3.2 Thickness estimation

Equations 4 and 5 were used to calculate the thickness of the germanium oxide obtained after successive heat treatments. By setting \( I_d^{\text{sub}} = I_{\text{Ge}2p} \) and \( I_d^{\text{ox}} = I_{\text{Ge}3d} \) in eq. 4, the thickness \( \delta_{2p} \) and in similar way \( \delta_{3d} \) refers to the use of Ge3d line. Furthermore, Ge2p an lines stemming from the substrate can be used to compute the oxide layer thickness by setting \( I_A = I_{\text{Ge}2p} \) and \( I_B = I_{\text{Ge}3d} \) in eq. 5, where \( I_A \) and \( I_B \) refer to Ge2p and Ge3d intensities. The value hence obtained is called \( \delta_{2p,3d} \). Notice that in the case of uniform layer, \( \delta_{2p}, \delta_{3d} \) and \( \delta_{2p,3d} \) should be equal.

The attenuation lengths \( \lambda_{2p} \) and \( \lambda_{3d} \) were estimated using expressions given in [7]. We obtained \( \lambda_{2p} = 5.3 \) and \( \lambda_{3d} = 12.3 \) monolayers (ML) [5]. The ratio \( I_{2p}^{2p} / I_{3d}^{3d} \) was found from a sputtered surface of germanium measurement to be 1.19. The two ratios \( I_{2p}^{2p} / I_{3d}^{2p} \) and \( I_{3d}^{3d} / I_{3d}^{3d} \) are evaluated from the slopes of \( I_{2p}^{2p} \) versus \( I_{3d}^{3d} \) plots: 0.68 [5]. With these values at hand, we computed the time evolution of the thickness.

The most conspicuous feature in Fig. 5 is the difference between the thickness obtained by different methods. In addition, \( \delta_{2p} \) and \( \delta_{3d} \) saturate at different levels an
decreases with time. Moreover, Figure 3 shows that the substrate signal is still present after a cumulated oxidation time exceeding 60 hours. This result suggests that parts of the surface are not or are slightly oxidized allowing the escape of the photoelectrons from the substrate. A substantial decrease of the oxidation rate is not likely because of the observation. The charge shift measured versus time is increasing which suggests the increase of the insulating oxide layer thickness; see Figure 6. In addition, it is noted that \( \delta_{2p} \) show some fluctuations in the plateau region consisting of a slight decrease in the thickness followed by a recovery or an increase in contrast with \( \delta_{2p,3d} \).

![Figure 6: The charge shift of C1s line from 284.5 eV binding energy](image)

The thickness fluctuations observed in Fig. 5 may be related to the mismatch between the atomic and oxide volume of the germanium atoms developing stresses that causes the layer to come off the surface during the cooling/heating cycles [5]. A value of \( \theta = 0.13 \) was estimated from the saturation levels of \( \delta_{2p} \) and \( \delta_{3d} \) in Figure 6. Using this value we have plotted the apparent thickness \( \delta_{2p} \), \( \delta_{3d} \) and \( \delta_{2p,3d} \) in terms of the real thickness in Figure 7. The time of oxidation and the real thickness resultant are functionally related and makes comparison of the experimental curves of Figures 5 and theoretical curves in Figure 7 permissible. The experimental saturation of \( \delta_{2p} \) and \( \delta_{3d} \) and the decrease of \( \delta_{2p,3d} \) are in agreement with the predictions of our model.

![Figure 7: Variation of apparent thickness \( \delta_{2p} \), \( \delta_{3d} \) and \( \delta_{2p,3d} \) in terms of the effective real thickness \( \delta \)](image)
4. Conclusion

The oxidation of (011) oriented Ge substrates under 380°C and 1atm pressure ambient been investigated using XPS technique. The experimental results suggest that the oxide XPS lines were composed of several peaks. These peaks correspond to the oxidation of germanium in accordance with high-resolution XPS studies. The values of the thickness that were calculated using the models of the literature showed a saturation decrease of the oxide thickness as the heat treatment duration increases. We have shown this unexpected behavior can be explained by assuming the growth of a non-uniform layer.

Acknowledgments

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References