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.

نمو طبقة الأكسيد فوق طبقة تحتية من أشباه الموصلات خطوة ذات أهمية كبيرة في عمليّة تصنيع مركّبات الحالة الصلبة. في هذا الورقة، استخدمنا مطيافيّة الإلكترونات لدراسة حركية نمو طبقات الأكسيدعلى سطح جيرمانيوم أحادي التبلور تحت ظروف تجريبيّة مختلفة .أجريت تجارب أكسدة داخل خليّة تسخين متصلة بمطياف الإلكترونات. تحليل الأطياف الإلكترونيّة يشير لنمو غير منتظم لطبقة الأكسيد. تم إقتراح نموذج يعرِّف سمكا ظاهريا لطبقة الأكسيد بدلالة السمك الحقيقي لجزر الأكسيد ونسبة السطح المغطّى بهذه الجزر. الأطياف الإلكترونيّة الملتقطة من زوايا مختلفة تدعم نموذجنا بقوّة.

1. Introduction

Studying thin layers on top of substrate is an important subject in oxidation/ corros chemical vapor deposition studies. The X-ray Photoelectron Spectroscopy (XPS) surface sensitive technique of choice for ultra-thin films (< 30 Angstroms). XP basically elemental and chemical information about the top layer of the surface. XPS in exciting a surface with x-rays of specified photon energy to excite the inner shell el of atoms. For the excited photoelectrons to emerge and be detected they must be comi within the top monolayers not deeper than few mean free paths or attenuation lengt what makes XPS a surface sensitive technique. The photoelectrons intensity versu 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 ox state of various elements. For a certain XPS line, the peaks that originate from the su atoms are distinguishable from the one from the oxide film. The quantitative analysis 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 meas 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 au 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 limits along with its application to the study of germanium oxide layers grown by oxidation.

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2. Thickness Estimation by XPS

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

2.1 Uniform Thickness Model

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

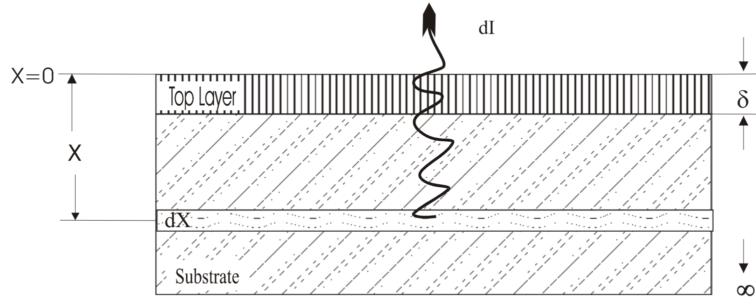


Figure 1: Uniform thickness estimation

The contribution *dI* of the slab *dx* to the emerging signal is given by:

$$dI = I^{*}(x)\exp(-x/\lambda)d(x/\lambda) \qquad (1)$$

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, λ attenuation length or the inelastic mean free path (IMFP). For simplicity, let us cons case of an oxide layer MO covering the surface of the metal M. Equation (1) integrated to evaluate the signals I_M^{sub} and I_M^{ox} coming from both the substrate and layer respectively:

$$I_M^{\ sub} = I^0 e^{(-\delta/\lambda)} \qquad (2)$$

$$I_M^{\ ox} = I^{\infty}(1 - e^{(-\delta/\lambda)}) \qquad (3)$$

Where I^0 and I^{∞} refer to the signals from a bare surface of the substrate and from an in thick layer of oxide (compared to λ). Equations 2 and 3 can be solved for δ:

$$\delta = \lambda \ln\left[\frac{I_M^{ox}}{I_M^{sub}}\frac{I^0}{I^{\infty}} + 1\right] \qquad (4)$$

The value of the attenuation length λ can be calculated for different materials us expression given by Seah and Dench [3]. The ratio I^0/I^{∞} can be obtained experiment combining Equations 2 and 3: $I_M^{ox} = I^{\infty} - (I^0/I^{\infty})\, I_M^{sub}$.

Furthermore, it is possible to use two XPS lines of the metal M of different energies (say A and B with IMFP λ_A and λ_B to estimate the thickness. The substrate s and B of Equation 2 can be rewritten for A and B to give:

$$\delta_{A,B} = \frac{\lambda_A}{1+\lambda_A/\lambda_B} \ln\left[\frac{I^{sub}_{M,B}}{I^{sub}_{M,A}}\frac{I^0_A}{I^0_B}+1\right] \quad (5)$$

This method requires the knowledge of the I^0_A/I^0_B 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 r be met in many practical cases [4]. For instance, let us assume that the layer is comp some islands with an average thickness δ covering part of the surface. The bare reg the surface constitute a fraction θ of the total surface as illustrated in Figure 2. Equa and 4 can be re-expressed as follows:

$$I^{sub}_M = \theta I^0 + (1-\theta) I^0 e^{(-\delta/\lambda)} \quad (6)$$

$$I^{sub}_M = (1-\theta) I^{\infty} (1-e^{(-\delta/\lambda)}) \quad (7)$$

For an assumed fixed value of the exposed fraction θ, we define the thickness obta using Equation 4 as the "apparent thickness". Using Equations 6 and 7, one obtains:

$$\delta_{apparent} = \lambda \ln\left[\theta + (1-\theta)e^{-\delta/\lambda}\right] \quad (8)$$

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

$$\delta = \lambda \ln\left[\frac{(1-\theta)}{\exp(-\delta_{apparnet}/\lambda)-\theta}\right] \quad (9)$$

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

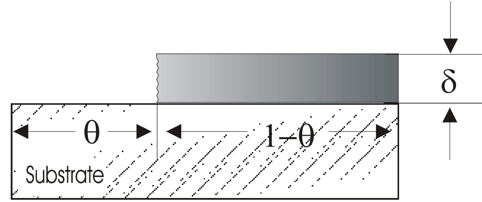


Figure 2: Layer of islands model

3 Germanium Oxidation

The oxidation of germanium substrates was investigated at 380°C under 1atm pres ambient air. Ge2p and Ge3d XPS lines were systematically collected after successi treatments of various durations. The experimental details are given elsewhere [5]. Tl spectra were obtained using an aluminum anode of 1486.6eV Kα x-ray line. The : regions including the $Ge2p_{3/2}$ (binding energy Eb=1217eV), Ge3d (29.6eV), ar (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 Ge2p$_{3/2}$ and Ge3d lines respectively und treatments for the indicated accumulated oxidation treatment time. The 1217eV energy peak is related to the substrate germanium (Ge^0), while the energies of the d possible oxidation states of germanium oxide top layer (Ge^{ox}) reside in the regior 1220eV. The Ge3d region has a main peak at 29.4 eV of elemental Ge beside a sm broad peak spanning the 31-34 eV range related to the oxidized Ge states. The signal the oxidized germanium (Ge^{ox}) clearly increases with the treatment time.

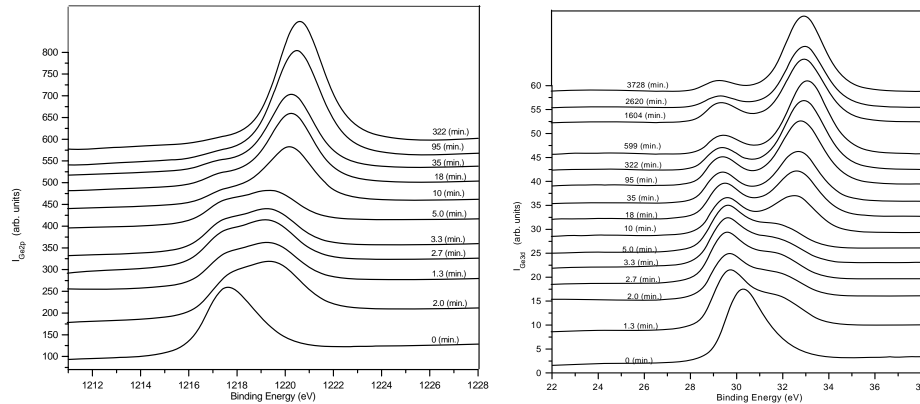
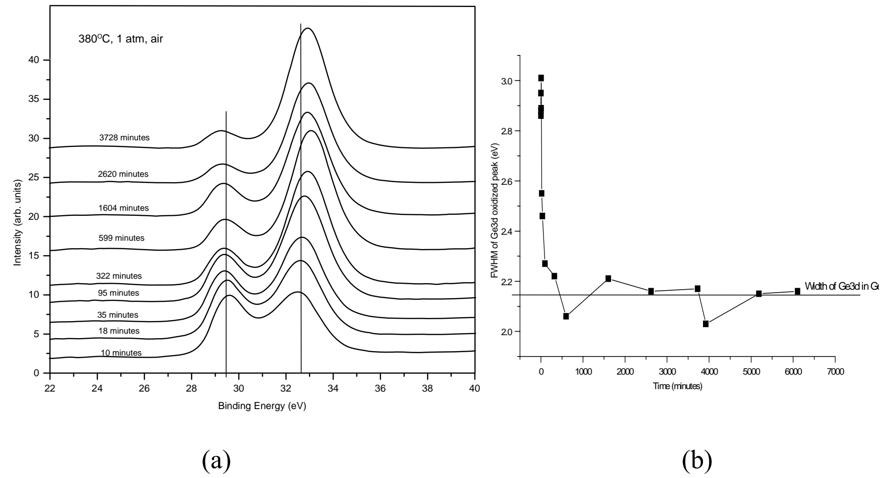


Figure 3: The progress of Ge2p$_{3/2}$ (a) and Ge3d (b) peak intensity distribution under oxidation

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

The assumption that we have four oxidation states is not a mere reliance literature as we have evidence that oxidation states exist. Figure 4(a) indicates t maximum of the oxidized peak shifts towards higher BE. This observation can be ex by the fact that the fourth oxidation state is increasing relative to the other states an shifts the maximum. If only two peaks are used to fit the experimental spectra, one o that the width of the oxidized peak is about 30% higher than that obtained from ger dioxide powder in the early oxidation stage. Subsequently, the width decreases and b closer to the GeO_2 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 oxid lines were computed and tabulated versus the accumulated oxidation treatment tim next step is to compute the oxide layer thickness progress using the above models.



(a) (b)

Figure 4: a) Width of the oxidized Ge3d peak progression under oxidation, b) The maximum of the o peak shifting to the higher BE with more oxidation time

3.2 Thickness estimation

Equations 4 and 5 were used to calculate the thickness of the germanium oxid obtained after successive heat treatments. By setting $I_M^{sub}= I_{Ge}^{2p}$ and $I_M^{ox}=I_{Ge}^{ox}$ in eq gets: δ_{2p} and in similar way δ_{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 b Eq. 5, where I_A and I_B refer to Ge2p and Ge3d intensities. The value hence obtained called $\delta_{2p,3d}$. Notice that in the case of uniform layer, δ_{2p}, δ_{3d} and $\delta_{2p,3d}$ should be equal.

The attenuation lengths λ_{2p} and λ_{3d} were estimated using expressions given [7]. We obtained λ_{2p} =5.3 and λ_{3d} =12.3 monolayers (ML) [5]. The ratio I^0_{2p}/ I^0_{3d} nee $\delta_{2p,3d}$ was found from a sputtered surface of germanium measurement to be 1.19. Th two ratios I^0_{2p}/ I^∞_{2p} and I^0_{3d}/ I^∞_{3d} are evaluated from the slopes of I^{ox} versus I^{Ge} plots: 0 0.68 [5]. With these values at hand, we computed the time evolution of the thickn Figure5.

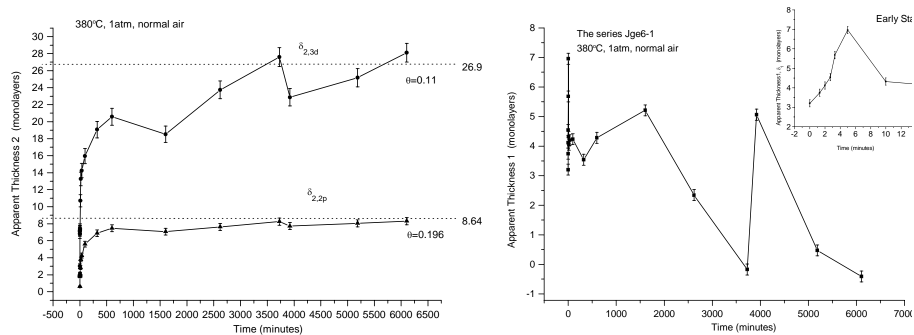


Figure 5: Uniform δ_{2p}, δ_{3d} and $\delta_{2p,3d}$ thickness versus time

The most conspicuous feature in Fig. 5 is the difference between the thickness obtained by different methods. In addition, δ_{2p} and δ_{3d} saturate at different levels an

decreases with time. Moreover, Figure 3 shows that the substrate signal is still prese after a cumulated oxidation time exceeding 60 hours. This result suggests that parts surface are not or are slightly oxidized allowing the escape of the photoelectrons fr substrate. A substantial decrease of the oxidation rate is not likely because of the fo observation. The charge shift measured versus time is increasing which suggests the i of the insulating oxide layer thickness; see Figure 6. In addition, it is noted that δ_{2p} show some fluctuations in the plateau region consisting of a slight decrease in the th followed by a recovery or an increase in contrast with $\delta_{2p,3d}$.

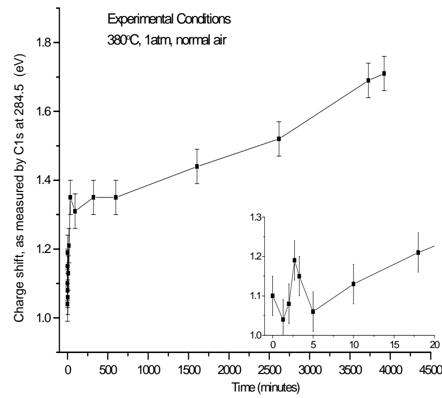


Figure 6: The charge shift of C1s line from 284.5 eV binding energy

The thickness fluctuations observed in Fig. 5 may be related to the mismatch b 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 θ e 0.13 was estimated from the saturation levels of δ_{2p} and δ_{3d} in Figure 6. Using this val we have plotted the apparent thickness δ_{2p}, δ_{3d} and $\delta_{2p,3d}$ in terms of the real thicknes Figure 7. The time of oxidation and the real thickness resultant are functionally relate makes comparison of the experimental curves of Figures 5 and theoretical curves in F permissible. The experimental saturation of δ_{2p} and δ_{3d} and the decrease of $\delta_{2p,3d}$ are agreement with the predictions of our model.

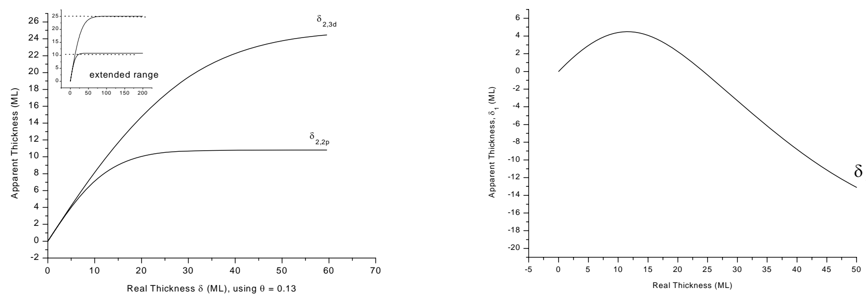


Figure 7: Variation of apparent thickness δ_{2p}, δ_{3d} and $\delta_{2p,3d}$ in terms of the effective real thickness δ

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 oxid
XPS lines were composed of several peaks. These peaks correspond to the oxidation s
germanium in accordance with high-resolution XPS studies. The values of the
thickness that were calculated using the models of the literature showed a saturati
decrease of the oxide thickness as the heat treatment duration increases. We have sho
this unexpected behavior can be explained by assuming the growth of a non-uniforr
layer.

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