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Pressure effect on the growth of oxide layers on germanium substrates

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Abstract

X-ray Photoelectron Spectroscopy (XPS) was used to investigate the growth of thin oxide layers obtained by dry oxidation on (*011*) germanium substrates. The heat treatments were carried out, in-situ, at $T = 380°C$ under various values of air pressure. The quantitative analysis of the XPS spectra suggests the growth of non uniform oxide layers. An apparent thickness of the oxide film was defined as function of the fraction of the oxidized surface and of the actual thickness of the oxide islands. The results show a quasi linear dependence of the apparent thickness versus the air pressure. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Germanium; Oxidation; XPS

1. Introduction

The growth of oxide layers on semiconductor substrates and the control of their properties is of crucial importance for microelectronics industry. Understanding the reaction of a solid surface to an oxidizing atmosphere is also a subject of fundamental interest. A considerable effort has been made to study the oxidation of silicon because of its use for the fabrication of most of solid state devices. Yet, the early stage of the oxidation mechanism remains a subject of debate [1]. Germanium has been much less studied despite its excellent electrical properties compared to silicon. This material was discarded for applications mainly because of its high cost and the instability of its oxide. However, its potential use in complementary metal oxide semiconductor (CMOS) elements and the development of Si/Ge multilayers based devices have induced an increasing interest for this material. The native oxide formed on chemically etched germanium surface at room temperature was characterized previously by Wei et al. using XPS [2]. Many authors studied the oxidation of germanium using various techniques [3,4]. In a previous work, we have used XPS to follow up the growth of oxide layers on germanium substrates under wet and dry atmospheres [5] and [6]. In this study we have investigated the effect of the air pressure on the growth kinetics of oxide layers obtained by dry oxidation of chemically etched samples.

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2. Experimental

Germanium samples were cut from a rod grown

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along the [*011*] direction. The surface perpendicular to the growth axis was mechanically polished with a diamond paste down to 1 μm size, then was chemically etched using CP4 solution ($HF:HNO_3:CH_3COOH$, 15:10:14 by volume) for 3 min. The samples were then rinsed with distilled water and stored in ethanol until they were place in the electron spectrometer (Type VG Escalab MKII). The heat treatments were carried out, in-situ, using a heating cell attached to the spectrometer. The air pressure varied from 0.05 to 760 Torr. All treatments were carried out at a fixed temperature ($T=380$°C). The XPS spectra were obtained using an aluminium anode producing a Kα X-ray line of 1486.6 eV energy. The spectral regions including the $Ge2p_{3/2}$ (binding energy $E_b=1217$ eV), Ge3d (29.6 eV), and O1s(532 eV) lines were scanned with 0.05 eV step size before and after each heat treatment. The C1s ($E_b=284.5$ eV) carbon line was used as a reference to perform the charge shift correction. The quantitative analysis of the spectra was performed by using a dedicated software based on the least squares method.

3. Results

Figs. 1 and 2 show the evolution of Ge2p3/2 and Ge3d lines respectively, after 15 min oxidation treatments at $T=380$°C under various air pressures ranging from 0.05 to 760 Torr. The 1217.5 eV binding energy peak (Ge2p) in Fig. 1 is related to the non oxidized germanium atoms while the peak appearing at 1220 eV ($Ge^{ox}2p$) refers to the oxidized atoms. Notice the clear increase of the $Ge^{ox}2p$ peak intensity at the expense of that of Ge2p as the air pressure increases. Similar trend can be observed also in Fig. 2 with a slower decrease of the non oxidized peak that remains clearly visible after the heat treatment under 760 Torr (Fig. 3, curve 9). The higher sensitivity of the $Ge2p_{3/2}$ line compared to

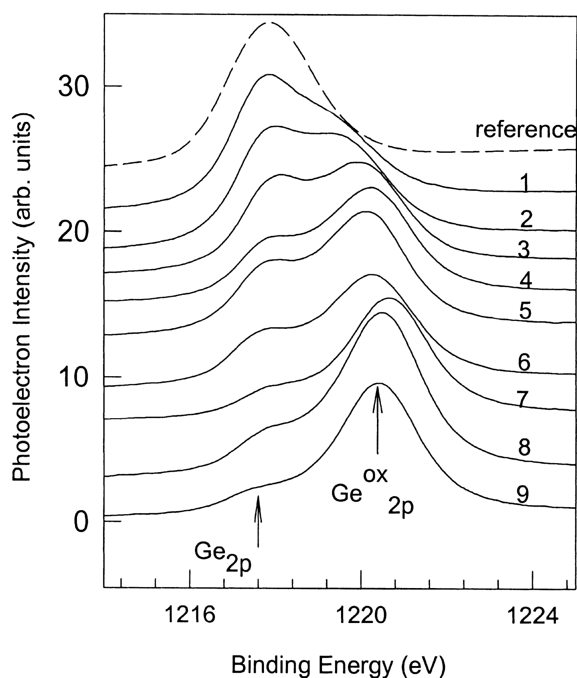


Fig. 1. $Ge2p_{3/2}$ line evolution after oxidation treatments during 15 min., at $T=380$°C. at different air pressures: $P=0.05$ Torr (1), 0.5 (2), 5 (3), 50 (4), 150 (5), 300 (6), 450 (7), 600 (8), 760 (9). Notice the increase of the intensity of the oxidized Ge peak at the expense of that of the non-oxidized atoms. The curve labeled as reference corresponds to the chemically etched surface prior to the oxidation treatment.

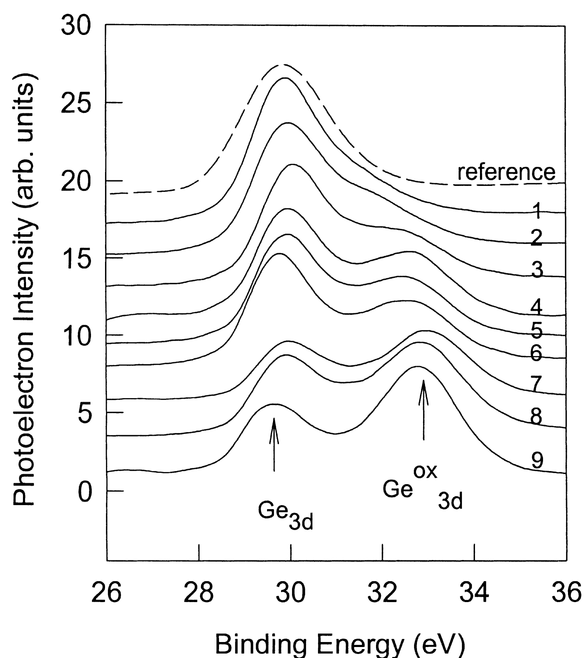


Fig. 2. Evolution of the Ge3d line after the same treatments as in Fig. 1. Notice the lower sensitivity of the Ge3d line to the oxidation compared to that of Ge2p line in Fig. 1. The curve labeled as reference corresponds to the chemically etched surface prior to the oxidation treatment.

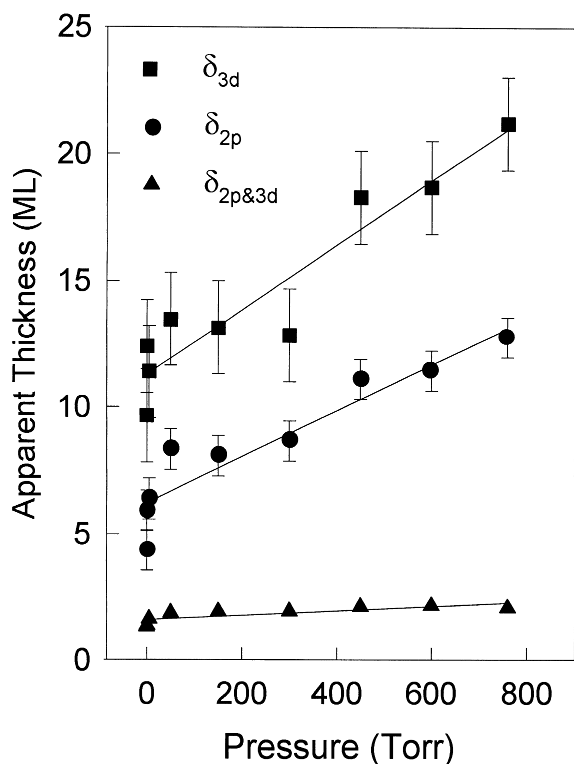


Fig. 3. Pressure Dependence of the apparent thickness δ_{2p} and δ_{3d} obtained by using Eq. (3) and $\delta_{2p}/3d$ obtained by using Eq. (4).

that of Ge3d is a consequence of the difference between their respective attenuation lengths λ_{2p} and λ_{3d} as discussed below.

4. Discussion

The increase of the signal originating from the oxidized atoms at the expense of that of the non oxidized ones that is observed in Figs. 1 and 2 indicates the growth of the oxide layer. XPS technique has been used by many authors to estimate the thickness of thin layers supported by different substrates [2,7]. The method is based on the Beer–Langmuir equation that gives the intensity of photoelectrons originating from the substrate as a function of the layer thickness. For instance, the intensity of photoelectrons that are collected from an infinitely thick germanium sample covered by an oxide layer of δ thickness, I_{Ge}, is given by:

$$I_{Ge} = I^0_{Ge} \exp\left(-\frac{\delta}{\lambda}\right) \quad (1)$$

where I^0_{Ge} is the intensity of the photoelectrons emitted from a Ge sample of a clean surface and where λ is the attenuation length of the photoelectrons. The distance λ is a function of the kinetic energy of the photoelectrons and can be calculated for different materials by using the expressions given in Ref. [8]. Similarly, the intensity of the photoelectrons originating from the oxidized atoms in the oxide layer, $I_{Ge^{ox}}$, is given by:

$$I_{Ge^{ox}} = I^{\infty}_{Ge^{ox}}\left[1 - \exp\left(-\frac{\delta}{\lambda}\right)\right] \quad (2)$$

where I^{∞}_{Ge} is the signal collected from an infinitely thick oxide sample.

By using Eqs. (1) and (2), one gets:

$$\delta = \lambda \, \mathrm{Ln}\left[1 + \frac{I_{Ge^{ox}} I^0_{Ge}}{I_{Ge} I^{\infty}_{Ge^{ox}}}\right] \quad (3)$$

The above method has been used by many authors to estimate the thickness of nanometric layers of silica on various substrates (see for example Refs. [7] and [9]). The main difficulty in this method is the determination of the ratio $I^0_{Ge}/I^{\infty}_{Ge^{ox}}$. A method has been suggested by Wang et al. [9] by pointing out that the slope of the graph $I_{Ge^{ox}}$ versus I_{Ge} is equal to $-I^{\infty}_{Ge}/I^0_{Ge^{ox}}$ and can be determined experimentally. A second method has been used by Wei et al. [2] to estimate the thickness of the native oxide layer obtained at room temperature on germanium samples. The method consists in comparing the intensities $I_{Ge2p_{3/2}}$ and I_{Ge3d}. The method takes advantage of the important difference between the binding energies of the two lines that leads to a significant difference between their respective attenuation lengths ($\lambda \; \alpha \; E^{1/2}$, E being the kinetic energy of the photoelectrons). By rewriting Eq. (1) for the lines $Ge2p_{3/2}$ and Ge3d and combining the two expressions one gets [5]:

$$\delta = \frac{\lambda_{2p}}{1 - \frac{\lambda 2p}{\lambda 3d}} \mathrm{Ln}\left[\frac{I_{Ge3d} I^0_{Ge2p}}{I_{Ge2p} I^0_{Ge3d}}\right] \quad (4)$$

Notice that one needs to perform an experimental determination of the factor I^0_{Ge2p}/I^0_{Ge3d} that correspond to ratio of the normalized areas of the $Ge2p_{3/2}$

and Ge3d peaks as measured from a clean surface. We have analyzed an argon sputtered surface and got a value equal to 1.7. In addition, by using the equations given in Ref. [8], we obtained the following values: $\lambda_{2p}=5.3$ML and $\lambda_{3d}=12.3$ML, where ML stands for monolayer.

It is important to notice that all these equations and, consequently, the above methods for thickness determination assume a layer of uniform thickness covering the whole surface of the sample. Using the first method based on Eq. (3) we have suggested in a previous work that this condition is not met in the case of germanium oxide layers grown by thermal oxidation of germanium substrates under dry and wet oxygen atmospheres [6]. The starting point of this suggestion is the observed difference between the thickness values that we have obtained using Eq. (1) for $Ge2p_{3/2}$ and Ge3d respectively. In this work, we have calculated the oxide layer thickness using both methods detailed above. The first method based on Eq. (1) gives two values δ_{2p} and δ_{3d} corresponding to the use of $Ge2p_{3/2}$ and Ge3d lines respectively. The second method based on Eq. (4) gives a third value that we refer to as $\delta_{2p/3d}$.

Fig. 3 shows the variation of the three values versus the air pressure. Notice the large discrepancy between the values obtained by different methods. In addition, one can notice the quasi linear increase of δ_{2p} and δ_{3d} versus the air pressure, while $\delta_{2p/3d}$ remains almost flat. The error bars reported in Fig. 3 have been estimated by using Eq. (3) and considering a 25% error on the coefficient $I^0_{Ge}/I^\infty_{Ge^{ox}}$ for the $Ge2p_{3/2}$ and Ge3d lines. Notice that the actual uncertainty on the thickness is slightly higher than that reported if we take into account the scatter of the experimental values the attenuation length given in Ref. [8] with a 1.38 standard deviation. However, as we are interested in comparing various methods using different XPS lines of the same element (Ge) to estimate the oxide thickness, the error on the attenuation lengths λ_{2p} and λ_{3d} was not considered.

In Ref. [6], we suggested the growth of the oxidation layer on the form of islands covering a fraction $(1-\theta)$ of the sample surface. In this case, Eqs. (1) and (2) can be rewritten on the following forms:

$$I_{Ge} = \theta I^0_{Ge} + (1-\theta) I^0_{Ge} \exp\left(-\frac{\delta}{\lambda}\right) \quad (5)$$

$$I_{Ge^{ox}} = (1-\theta) I^\infty_{Ge^{ox}} \left[1-\exp\left(-\frac{\delta}{\lambda}\right)\right] \quad (6)$$

The use of Eqs. (3) and (4) leads to different 'apparent thickness', δ_{app}, that can be expressed in terms of the actual thickness of the islands δ, and the fraction θ by rewriting Eqs. (3) and (4) as follows:

$$\delta_{app}(2p) = \lambda_{2p}\,\mathrm{Ln}\left[x_{2p} + (1-x_{2p})\theta\right] \quad (7)$$

$$\delta_{app}(3d) = \lambda_{3d}\,\mathrm{Ln}\left[x_{3d} + (1-x_{3d})\theta\right] \quad (8)$$

$$\delta_{app}(2p/3d) = \frac{\lambda_{2p}}{1-\dfrac{\lambda 2p}{\lambda 3d}}\,\mathrm{Ln}\left[\frac{\theta + (1-\theta)x_{3d}}{\theta+(1-\theta)x_{2p}}\right] \quad (9)$$

where

$$x_{2p,3d} = \exp\left(-\frac{\delta}{\lambda_{2p,3d}}\right).$$

Fig. 4 shows the variation of the three apparent thicknesses as a function of the actual thickness of the islands for a fixed value of $\theta = 10\%$. Let us point out two results of the model that strongly support the interpretation of our experimental results. First, the model predicts $\delta_{app}(3d) > \delta_{app}(2p) > \delta_{app}(2p/3d)$ as observed experimentally. Second, the variation of $\delta_{app}(2p/3d)$ saturates and may even decrease as the actual thickness of the oxide islands increases beyond 15ML. In addition, we have carried out angle resolved XPS analyses after a 5-min treatment at $T=380$°Cunder 300 Torr air pressure. The results are reported in Fig. 5. The angular dependence of the apparent thickness can be obtained from Eq. (7) provided the actual thickness δ is replaced by $\delta/(\sin\alpha)$, α being the take-off angle of photoelectrons. Notice that for a uniform layer ($\theta = 0$), Eq. (7) gives $\delta_{app} = \delta/(\sin\alpha)$. Fig. 5 shows a clear departure from linearity of the graph δ_{app} versus $1/(\sin\alpha)$. Furthermore, the experimental data are well fitted using Eq. (7).

The good agreement between the model and the experimental data reported in Figs. 3 and 5 strongly supports the growth of non uniform oxide layers on the substrate. In a recent work, Ying et al. [10] used Atomic Force Microscopy (AFM) to observe the microstructure of the oxide films grown under air at room temperature on heavily doped silicon sub-

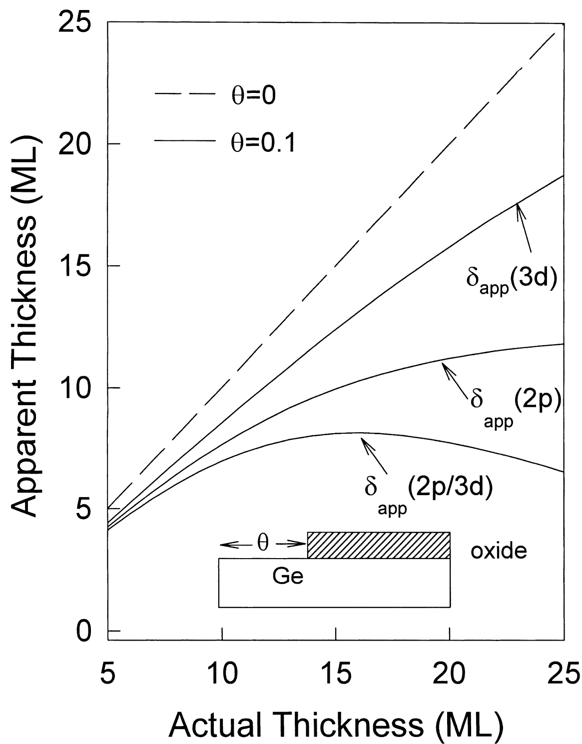
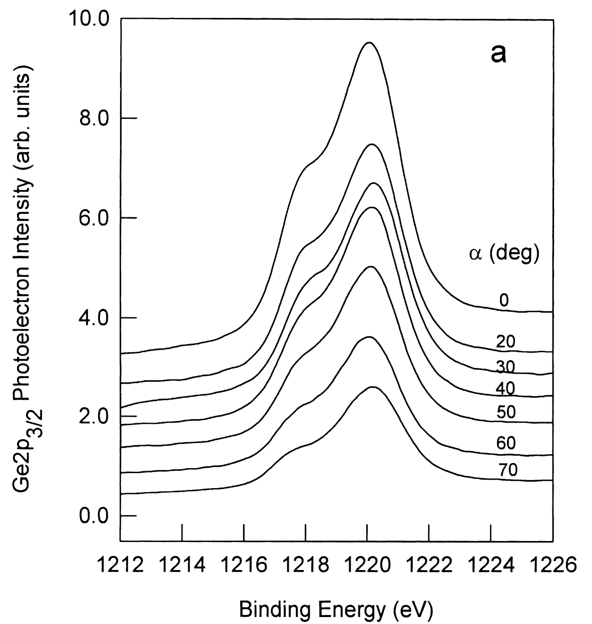


Fig. 4. Variation of the apparent thickness versus the actual thickness of the oxide islands covering a fraction $(1-\theta)$ of the surface. Notice that for $\theta=0$ (full coverage of the surface by a uniform oxide layer), the three methods lead to the same value $\delta_{app}=\delta$ (actual).

strates. The images revealed a geometrical pattern which consists of various-sized plateaus of 2 nm average height. The AFM technique would certainly provide a useful information that will help to achieve a better understanding of the oxidation process of germanium.

5. Conclusion

The oxidation of germanium substrates under various air pressures was investigated using X-ray Photoelectron Spectroscopy. Three methods were considered to estimate the apparent thickness of the oxide layers using the XPS data. The discrepancy between the values obtained by the three methods was explained by assuming the formation of oxide islands that cover partially the surface of the substrate. The results show a linear increase of the apparent thickness as the air pressure increases.



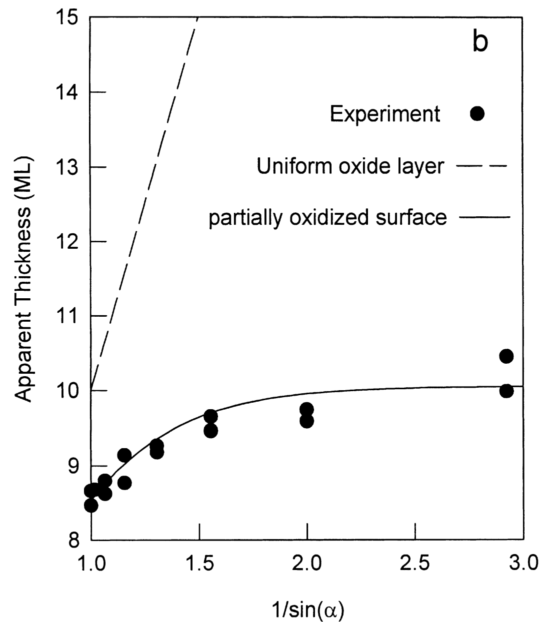


Fig. 5. Variation of the apparent thickness versus the take-off angle. The continuous line corresponds to $\theta=0.15$ and $\delta=15$ML.

Acknowledgements

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