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Spectroscopic Ellipsometric Measurements of the Dielectric Function of Germanium Dioxide Films on Crystal Germanium

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SPECTROSCOPIC ELLIPSOMETRIC MEASUREMENTS OF THE DIELECTRIC FUNCTION OF GERMANIUM DIOXIDE FILMS ON CRYSTAL GERMANIUM

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ABSTRACT

From spectroscopic ellipsometry measurements in the 1.5 to 5.7 eV photon energy range we determined the complex dielectric function of thermally grown germanium dioxide in the 1.0 to 6.3 eV range. A Kramers-Kronig consistent dispersion formula utilizing an exponential shaped optical band edge was used in conjunction with both previously published far ultraviolet absorbance data for amorphous GeO_2 and our spectra. These measurements show that ε_2 for GeO_2 can be regarded to be zero in the range of $E<5.5$ eV, which differs from a previous report. Using this new optical results for the investigation of oxide growth, we find that GeO_2 grows via a parabolic growth law with a growth constant, $k_p=1.2\ 10^{-19}\ m^2s^{-1}$ at 550 °C.

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Demands for faster metal-oxide-semiconductor devices have led to investigations of novel device structures and materials systems. Because of the large hole mobility in Ge and less disparate hole and electron mobilities than in other semiconductors, particularly at low temperatures, Ge emerges as an attractive candidate semiconductor for microelectronic technology[1,2,3]. Consequently, interest is revived in obtaining a high quality insulator film on the Ge surface. In order to study GeO_2 film formation and properties, it is required to have the GeO_2 film dielectric function in a wide spectral range . A method for this measurement and data for thermally prepared GeO_2 film is the subject of the present research.

In 1969 Pajasová[4] determined the optical constants of amorphous and crystalline GeO_2 in the 1.0 to 24 eV spectral range from reflectivity measurements and with the use of Kramers-Kronig analysis. But limitations of this technique and/or impurities in their bulk samples yielded in high optical absorbance in the 2.0 to 6.5 eV region. Recently, Boháč et al.[5] measured the optical properties of rf magnetron sputtered and post annealed GeO_2 layers. But the simplified analysis technique used to interpret the reflectance and transmittance data yielded additional absorbance features and did not give sufficient dielectric function information in the entire spectral range.

In this paper we report the spectroscopic ellipsometric (SE) characterization of thermally grown germanium oxides on single-crystal germanium substrates in the energy range of 1.5 to 5.7 eV. A novel Kramers-Kronig consistent dispersion formula that is based on the main spectral features cf the amorphous GeO_2 far ultraviolet (FUV) absorbance spectrum[4], and utilizing an exponential shaped optical band edge, precisely fits both our

spectra and previously published absorbance data. This procedure is valid in the entire range between hydrogen related absorbance in the near infrared near 1 eV and to about 6.3 eV, were the detailed structure of the UV absorbance must be taken in account.

The ellipsometric measurements were carried using a previously described home made rotating analyzer spectroscopic ellipsometer[6] operating in the energy range 1.5 to 5.7 eV. All the measurements were performed at an incidence angle of 70.0^0. The offsets of polarizer and analyzer were determined for each sample[7] and an optical filter cut off at 350 nm was used for measurements below 2.5 eV.

Germanium oxide films were thermally grown on commercially available single crystal (111) germanium substrates. All Ge substrates were subjected to a pre-oxidation cleaning procedure as previously described by Aspnes[8] and which consists of 0.05-vol% bromine in methanol etch, followed by a buffered HF cleaning step and a final deionized water rinsing. The bromine methanol etch step was intended to minimize residual layers at the surfaces. The latter is further stripped by the buffered HF solution, which renders the surface stable prior to oxidation. The thermal oxidation was performed at 550 ^oC at 1 atm in dry flowing O_2 gas in a conventional double-walled fused silica oxidation furnace. Prior to the oxidation furnace the O_2 was flowed through a preburner-condenser apparatus described by Irene[9] and films were grown in the 4 to 70 nm range.

Spectroscopic ellipsometry provides the spectra of $\tan\Psi$ and $\cos\Delta$ where Ψ and Δ are the ellipsometric angles that describe the reflection of polarized light from the sample. These spectra have to be compared with modelled spectra calculated from the geometrical and optical parameters of the sample. For our GeO_2-Ge-structures we consider a stratified three

phase model (ambient/GeO_2/Ge substrate) to be justified below. Consequently we have: $\tan\Psi = |\rho|$; $\cos\Delta = \arg(\rho)$ with $\rho = r_p/r_s = f(E, \varepsilon_f, L_f, \varepsilon_s, \phi)$ where r_p and r_s are the complex reflectivities of the sample and are calculated with an appropriate matrix algorithm[10]. The photon energy, E, and the angle of incidence, ϕ, are known parameters of the measurement and ε_s, the complex dielectric function of the substrate[11], are supplied to the calculation. This leaves ε_f, the film dielectric function and L_f, the film thickness of the GeO_2 layer as parameters to be determined from the experimental spectra. Using an appropriate dispersion formula $\varepsilon_f(E)$ with the number of adjustable parameters equal to k and the number of parameters, $q_1,...,q_M$, to be fitted to the measured spectra each with N spectral points is reduced to M=1+k. These M parameters are determined by the minimization of the error weighted sum of squares, S, given as:

$$S = \frac{1}{2N-M-1}\sum_{i=1}^{N}\left(\frac{\tan\psi_{cal}(q_1,...,q_M)-\tan\psi_{exp}}{\delta\tan\psi_{exp}}\right)^2+\left(\frac{\cos\Delta_{cal}(q_1,...,q_M)-\cos\Delta_{exp}}{\delta\cos\Delta_{exp}}\right)^2 \quad (1)$$

In order to reduce the systematic errors and to keep the fraction M/2N as small as possible, the dispersion relation for GeO_2 has two requirements: it must adequately represent the real dispersion, and it must use as small a number of parameters as possible. Following the arguments of Pikhin and Yaskov[12] and using the data given by Pajasová[4] for glassy GeO_2, we construct the following dispersion formula with reference to Figure 1:

$$\varepsilon_1(E) = 1 + \frac{A}{\pi}\int_0^{E_1}\frac{E^* e^{\frac{E-E_1}{E_u}}}{E^{*2}-E^2}dE^* + \frac{A}{\pi}\ln\frac{E_2^2-E^2}{E_1^2-E^2} \tag{2}$$

The logarithmic term results from a step function shaped approximation of the mean UV absorption between energies E_1 and E_2, and the integral term gives the ε_1 contribution of the absorption tail at $E<E_1$, that is assumed to be exponential with a characteristic decay energy, E_u. The exponential contribution can be calculated by fitting the exponential shape of ε_2 with a cubic spline, because then all of the resulting integrals have integrands of the type $E^{*i}/(E^{*2}-E^2)$, i=1,..,4 for which analytic solutions are given[13]. With the E_1 position fixed at the low energy absorption peak at 6.8 eV, eqn(2) meets the above mentioned requirements and results in a total number of only four parameters (L_f, A, E_u, E_2) to fit our $\tan\Psi$ and $\cos\Delta$ spectra with N number of data points where N is about 100. The main advantage of eqn(2) is the applicability to the transition between transparent and absorbing regions of amorphous materials.

According to Humlíček[14] the standard deviation $\delta^s q_j$ of the parameters $q_1,...,q_M$ used to fit the experimental spectra can be calculated with the relationships:

$$\delta^s q_j = \sqrt{H^{-1}_{jj}} \text{ with } H_{ij} = \frac{1}{2}\frac{\partial^2 S}{\partial q_i \partial q_j} \text{ and } i,j = 1,...,M \tag{3}$$

where H is the Hessian matrix of our minimization problem. For both, minimization and error calculation, the statistical errors $\delta\tan\Psi$ and $\delta\cos\Delta$ are needed. They are calculated from the well known expressions[15], that relate the ellipsometric angles to the measured Stokes parameters, s_0, s_1, and s_2, which are further related to the statistical error of the

intensity measurement $\delta I/I$. Consequently, we use:

$$\frac{\delta \tan\Psi}{\tan\Psi} = \frac{1}{2}\left(\tan\Psi + \frac{1}{\tan\Psi}\right)^2 \frac{\delta I}{I} \tag{4}$$

$$\delta\cos\Delta = \frac{1}{2}\left[(\tan\Psi + \frac{1}{\tan\Psi}) + |\cos\Delta|\right]\frac{\delta I}{I} + |\cos\Delta|\frac{\delta\tan\Psi}{\tan\Psi}$$

as statistical errors of the ellipsometric measurements and weighting parameters for the calculation of S. The upper limits of systematic errors $\delta^f q_j$ due to the uncertainties of the fixed parameters, ϕ and ε_s, were also calculated using an extended Hessian matrix[14]. In the following we use for the total error δq_j of the parameters resulting from the minimization procedure: $\delta q_j = |\delta^s q_j| + |\delta^f q_j|$.

A series of GeO_2 films thicknesses ranging from 60 to 70 nm were thermally grown. The samples were measured by SE in the 1.5 - 5.7 eV spectral range immediately following the oxidation. The results from the above procedures for three typical samples are summarized along with S values near unity in Table 1.

In Figure 2a the experimental $\tan\Psi$ and $\cos\Delta$ spectra of sample #2 are compared to the best fit spectra which was calculated according to eqns. (1) and (2) and using the values in Table 1 which were derived from the data. The resulting dispersion of ε_f for GeO_2 (A=2.46 , E_u=0.17 eV, E_2=17.6 eV) is shown in Fig.2b, and the included error range indicates the influence of δA, δE_u and δE_2. In order to facilitate comparison with previous results, experimental ε_1 and ε_2 values from references 4 and 5 are added. In Fig.1, where the physical meaning of our dispersion formula was illustrated, the ε_2 data from references 4 and 5 are also given. Even though we do not actually measure the absorbance of GeO_2, because it is too small to be measured with ellipsometry for E<6 eV, our dispersion model

yields information about the absorbance band edge that is in excellent agreement with the data of Boháč et al[5]. The decrease in ε_2, measured[5] for E>6.2 eV, we regard as an artefact resulting from an incorrect refractive index extrapolation. The paper of Pajasová[4] precisely locates the energy positions for the main absorbance features in the FUV, but for E<6.7 eV it gives an ε_2 value that is too large; and this may be related to limitations of the Kramers-Kronig analysis technique used for their reflectance spectra of glassy bulk GeO_2.

The precise values of ε_1 and ε_2 as now determined can be used to evaluate the GeO_2 film growth data in terms of a two layer optical model. One layer being the GeO_2 film and the other an interface region. Results here which model the interface as an effective medium with a-Ge and GeO_2 as constituents has a thickness of $L=0.5 \pm 0.2$ nm. For the case of the thicker GeO_2 films used in this study this small extent of the interface region will not seriously effect either the film thickness or the dispersion parameters determined above.

For our work only the spectral region E<5.5eV is of interest, where for ellipsometric measurements ε_2 of GeO_2 can be regarded to be zero, the integral term in eqn.(2) can be dropped and $\varepsilon_1(E)$ can be fitted using only the logarithmic term with A=2.37, E_1=6.55 eV, and E_2=18.0 eV. Using the dielectric function of thermal GeO_2, we analyzed a set of Ge samples oxidized for 0.2-11 hours at 550 ^oC in dry O_2. The results are given in Fig.3 and and are well described by a parabolic rate law: $L^2 = k_p t$ and previous data[1] are also in substantial agreement. The temperature-dependent growth constant k_p was found to be 1.2×10^{-19} m^2S^{-1} at 550 ^oC.

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FIGURE CAPTIONS

Figure 1

Shape of the simplified FUV dielectric function (solid lines) that is used for our dispersion formula for the dielectric function of GeO_2 in the vis-UV region. The parameters (A=2.46 , E_u=0.17 eV, E_2=17.6 eV) result from a fit only to our SE measurements in the 1.5 to 5.7 eV spectral range.

Figure 2

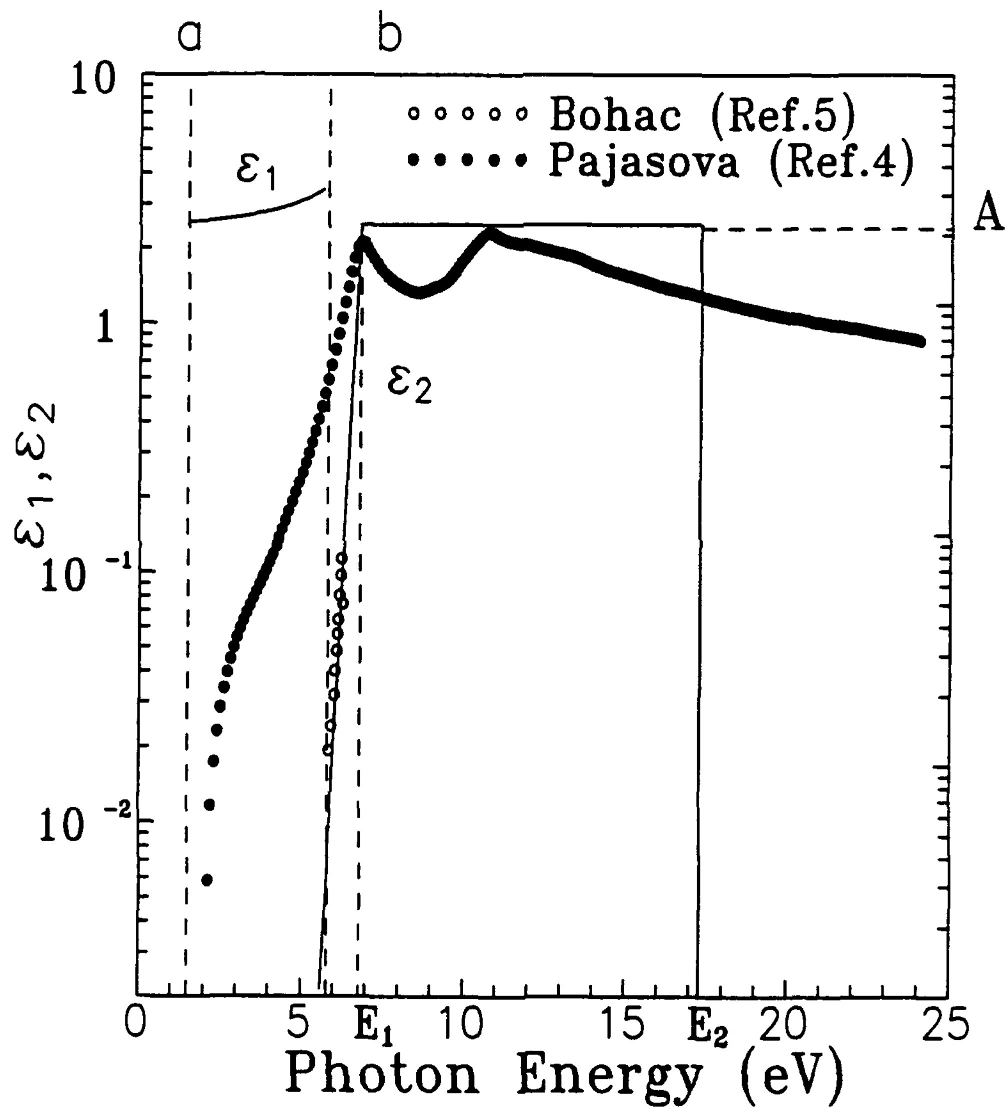
Ellipsometric measurement of GeO_2 dielectric function: a) $\tan\Psi$ and $\cos\Delta$ spectra of sample #2: experiment (dotted) and best fit (line). b) ε_1 and ε_2 of GeO_2 according to eqn.(2) with A=2.46, E_u=0.17 eV, E_2=17.6 eV.

Figure 3

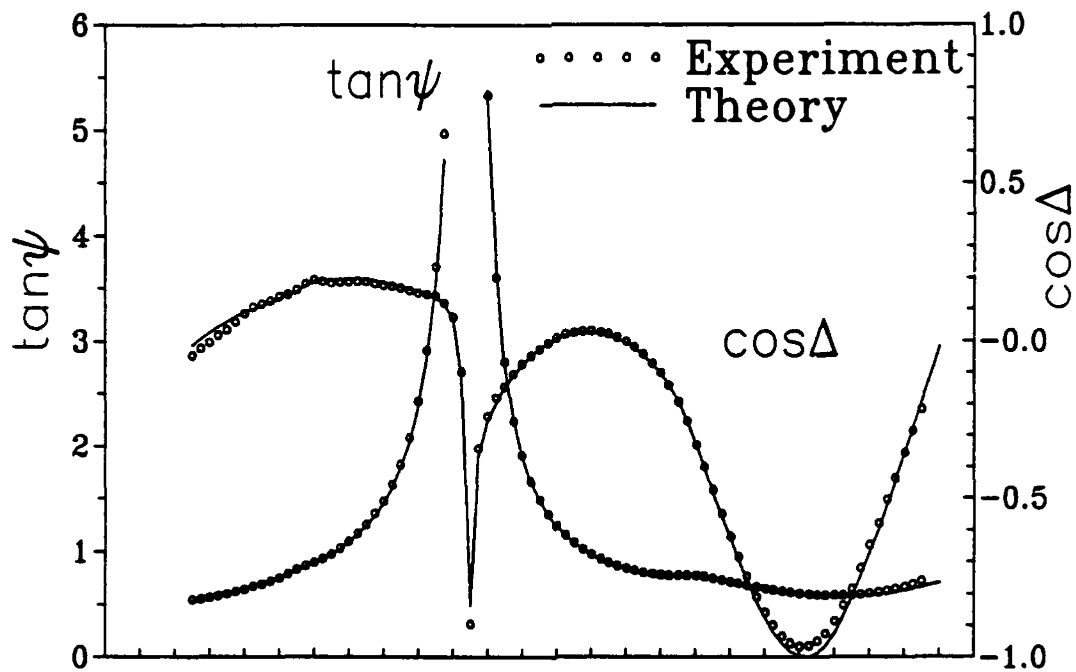
Square of GeO_2 film thickness vs. the thermal oxidation time obtained from ellipsometric measurements at 550 ^oC.

Table I. The adjustable parameters of three typical samples.

Sample	d_f (nm)	A	E_u (eV)	E_2 (eV)	S value
#1	60.5 ± 0.5	2.41 ± 0.08	0.18 ± 0.04	17.3 ± 0.3	1.2
#2	67.2 ± 0.3	2.49 ± 0.05	0.17 ± 0.03	17.6 ± 0.3	0.4
#3	63.2 ± 0.3	2.44 ± 0.05	0.17 ± 0.03	17.6 ± 0.5	0.4



a
b
10
1
10^{-1}
10^{-2}
$\varepsilon_1, \varepsilon_2$
ε_1
ε_2
Bohac (Ref.5)
Pajasova (Ref.4)
A
0
5
E_1
10
15
E_2
20
25
Photon Energy (eV)


Experiment
Theory
tanψ
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0
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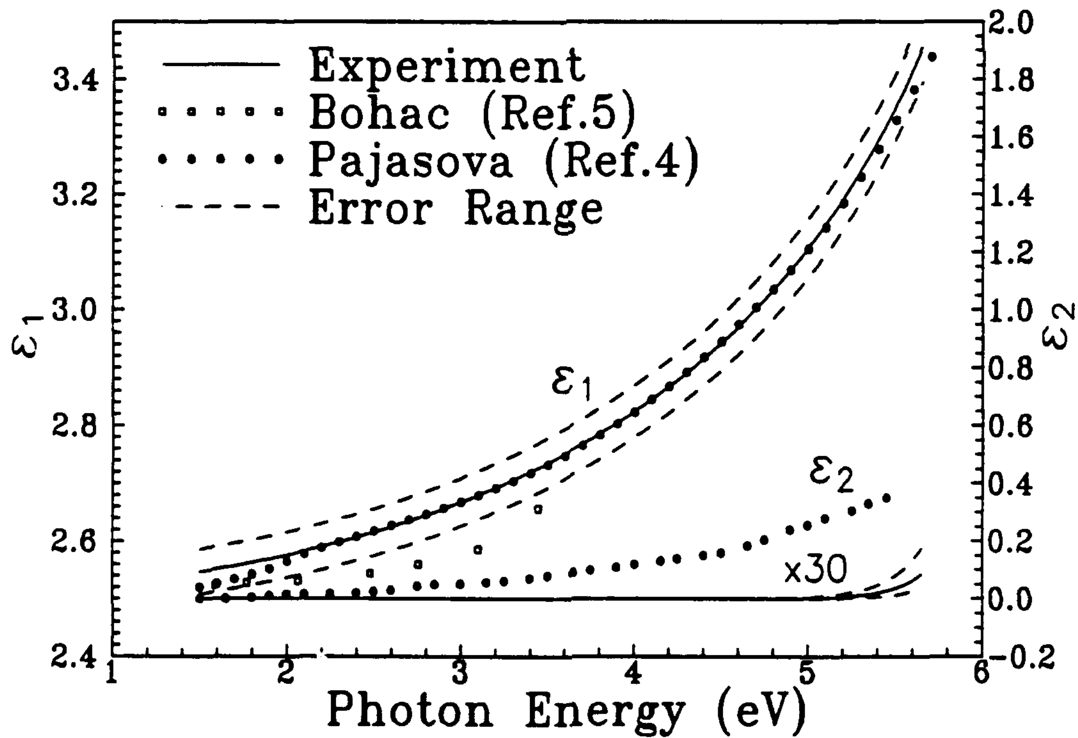
Experiment
Bohac (Ref.5)
Pajasova (Ref.4)
Error Range
ε1
ε2
x30
Photon Energy (eV)
1
2
3
4
5
6
2.4
2.6
2.8
3.0
3.2
3.4
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1.8
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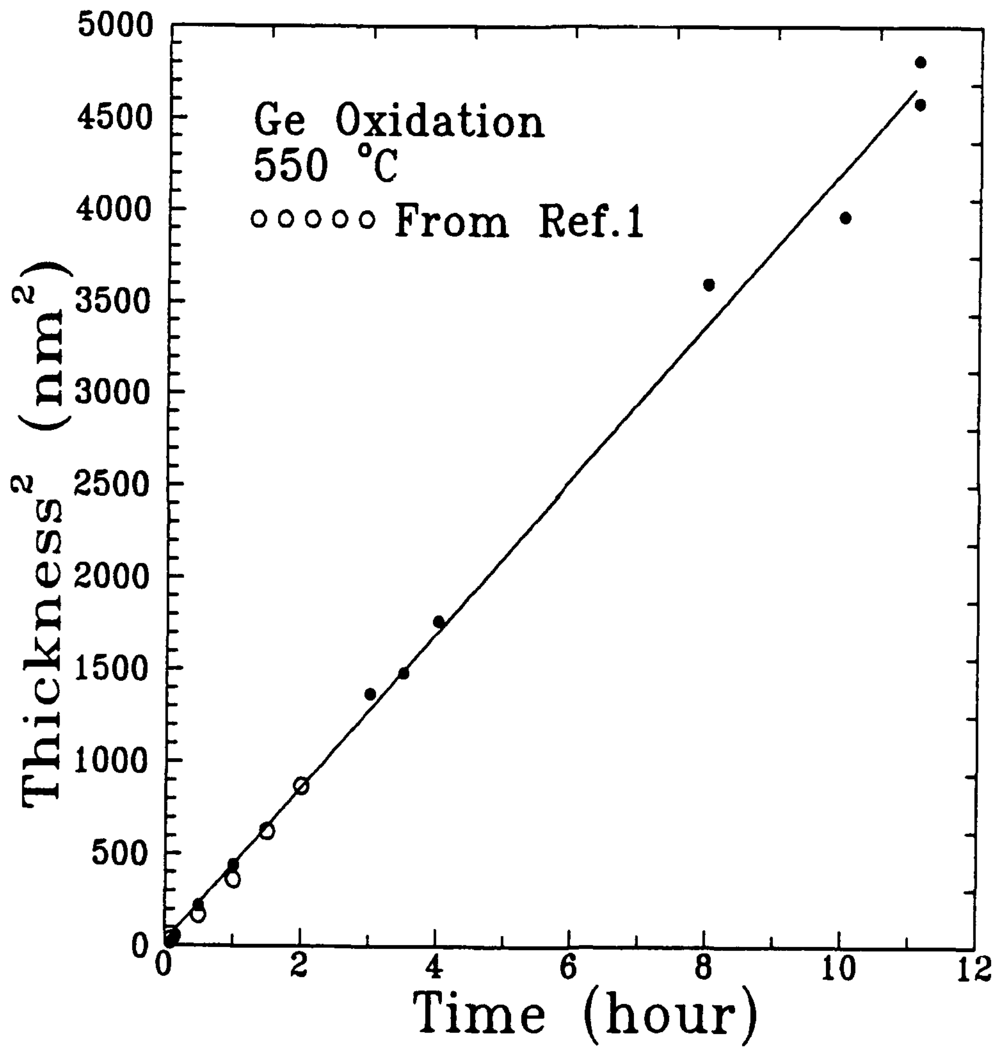
0.2
0.0
-0.2


Ge Oxidation
550 °C
oooooo From Ref.1
Thickness^2 (nm^2)
Time (hour)
0
500
1000
1500
2000
2500
3000
3500
4000
4500
5000
0
2
4
6
8
10
12