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13. ABSTRACT (Maximum 200 words)

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

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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\textsuperscript{1,2,3}. Consequently, interest is revived in obtaining a high quality insulator film on the Ge surface. In order to study GeO\textsubscript{2} film formation and properties, it is required to have the GeO\textsubscript{2} film dielectric function in a wide spectral range. A method for this measurement and data for thermally prepared GeO\textsubscript{2} film is the subject of the present research.

In 1969 Pajasová\textsuperscript{4} determined the optical constants of amorphous and crystalline GeO\textsubscript{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.\textsuperscript{5} measured the optical properties of rf magnetron sputtered and post annealed GeO\textsubscript{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 of the amorphous GeO\textsubscript{2} far ultraviolet (FUV) absorbance spectrum\textsuperscript{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 operating in the energy range 1.5 to 5.7 eV. All the measurements were performed at an incidence angle of 70.0°. The offsets of polarizer and analyzer were determined for each sample 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 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 °C at 1 atm in dry flowing O2 gas in a conventional double-walled fused silica oxidation furnace. Prior to the oxidation furnace the O2 was flowed through a preburner-condenser apparatus described by Irene and films were grown in the 4 to 70 nm range.

Spectroscopic ellipsometry provides the spectra of tanΨ and cosΔ 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 GeO2-Ge-structures we consider a stratified three
phase model (ambient/GeO$_2$/Ge substrate) to be justified below. Consequently we have: 
\[ \tan \Psi = |\rho|; \cos \Delta = \text{arg}(\rho) \] with \( \rho = \frac{r_p}{r_s} = f(E, \varepsilon_f, L_f, \varepsilon_s, \phi) \) where \( r_p \) and \( r_s \) are the complex reflectivities of the sample and are calculated with an appropriate matrix algorithm\textsuperscript{10}. The photon energy, \( E \), and the angle of incidence, \( \phi \), are known parameters of the measurement and \( \varepsilon_s \), the complex dielectric function of the substrate\textsuperscript{11}, are supplied to the calculation. TL's leaves \( \varepsilon_f \) 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, \( q_1, \ldots, q_M \), 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:

\[ S = \frac{1}{2N-M-1} \sum_{i=1}^{N} \left( \frac{\tan \Psi_{\text{cal}}(q_1, \ldots, q_M) - \tan \Psi_{\text{exp}}}{\delta \tan \Psi_{\text{exp}}} \right)^2 \left( \frac{\cos \Delta_{\text{cal}}(q_1, \ldots, q_M) - \cos \Delta_{\text{exp}}}{\delta \cos \Delta_{\text{exp}}} \right)^2 \] (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\textsuperscript{12} and using the data given by Pajasová\textsuperscript{4} for glassy GeO$_2$, we construct the following dispersion formula with reference to Figure 1:
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 $e_1$ contribution of the absorption tail at $E < E_1$, that is assumed to be exponential with a characteristic decay energy, $E_\mu$. The exponential contribution can be calculated by fitting the exponential shape of $e_2$ 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. 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 ($Lp, A, E_\mu, E_2$) 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 the standard deviation $\delta q_j$ of the parameters $q_1,...,q_M$ used to fit the experimental spectra can be calculated with the relationships:

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

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, 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:

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

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

as statistical errors of the ellipsometric measurements and weighting parameters for the calculation of $S$. The upper limits of systematic errors $\delta^0 q_j$ due to the uncertainties of the fixed parameters, $\phi$ and $e$, were also calculated using an extended Hessian matrix. In the following we use for the total error $\delta q_j$ of the parameters resulting from the minimization procedure:

$$\delta q_j = |\delta^0 q_j| + |\delta^f q_j|.$$

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 $e_f$ 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 $\delta A$, $\delta E_u$ and $\delta E_2$. In order to facilitate comparison with previous results, experimental $e_I$ and $e_2$ values from references 4 and 5 are added. In Fig.1, where the physical meaning of our dispersion formula was illustrated, the $e_2$ 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\textsuperscript{5}. The decrease in $\varepsilon_2$, measured for $E > 6.2$ eV, we regard as an artefact resulting from an incorrect refractive index extrapolation. The paper of Pajasová\textsuperscript{4} precisely locates the energy positions for the main absorbance features in the FUV, but for $E < 6.7$ eV it gives an $\varepsilon_2$ 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 $\varepsilon_1$ and $\varepsilon_2$ 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 $E < 5.5$ eV is of interest, where for ellipsometric measurements $\varepsilon_2$ 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 °C in dry O$_2$. The results are given in Fig.3 and are well described by a parabolic rate law: $L^2 = k_p t$ and previous data\textsuperscript{7} are also in substantial agreement. The temperature-dependent growth constant $k_p$ was found to be $1.2 \times 10^{-19}$ m$^2$ S$^{-1}$ at 550 °C.

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REFERENCES.

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 ($A=2.46\,\text{eV}$, $E_u=0.17\,\text{eV}$, $E_2=17.6\,\text{eV}$) 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) $\varepsilon_1$ and $\varepsilon_2$ of GeO$_2$ according to eqn.(2) with $A=2.46\,\text{eV}$, $E_u=0.17\,\text{eV}$, $E_2=17.6\,\text{eV}$.

Figure 3

Square of GeO$_2$ film thickness vs. the thermal oxidation time obtained from ellipsometric measurements at 550 °C.
Table I. The adjustable parameters of three typical samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$d_f$ (nm)</th>
<th>A</th>
<th>$E_u$ (eV)</th>
<th>$E_2$ (eV)</th>
<th>S value</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>60.5 ± 0.5</td>
<td>2.41 ± 0.08</td>
<td>0.18 ± 0.04</td>
<td>17.3 ± 0.3</td>
<td>1.2</td>
</tr>
<tr>
<td>#2</td>
<td>67.2 ± 0.3</td>
<td>2.49 ± 0.05</td>
<td>0.17 ± 0.03</td>
<td>17.6 ± 0.3</td>
<td>0.4</td>
</tr>
<tr>
<td>#3</td>
<td>63.2 ± 0.3</td>
<td>2.44 ± 0.05</td>
<td>0.17 ± 0.03</td>
<td>17.6 ± 0.5</td>
<td>0.4</td>
</tr>
</tbody>
</table>
\[ \tan \psi \]

**Experimental vs. Theoretical Results**

- **Experiment**
- **Bohac (Ref. 5)**
- **Pajasova (Ref. 4)**
- **Error Range**

**Graph 1:**
- Photon Energy (eV)
- \( \tan \psi \) vs. \( \cos \Delta \)

**Graph 2:**
- \( \varepsilon_1 \) vs. \( \varepsilon_2 \)
- \( \varepsilon_1 \) and \( \varepsilon_2 \) vs. Photon Energy (eV)
Ge Oxidation
550 °C
○○○○ From Ref.1