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Characterisation of Thin Surface Films on Germanium in Various Solvents by Ellipsometry

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Ellipsometric techniques were used to investigate the thin films that formed on cleaved germanium samples in air, deionised water, and 30% hydrogen peroxide. In all three cases the films were less than 100 Å in thickness. The films formed in air and water had a refractive index of 1.63 ± 0.02 which is close to that of glassy GeO_2. An increase of refractive index to about 1.74 was observed when the samples were immersed in a solution of 30% H_2O_2. The thickness of this film (18Å) remained relatively constant in a period of 5 min to 6 h. The film is attributed to a layer of $Ge(OH)_2^{2+}$ surface complexes, and a thick reaction envelope of metagermanic acid (H_2GeO_3). After rinsing surfaces covered with glassy GeO_2 with a 48% HF solution, the original oxide was removed; however, within 5 min a 50Å thick film of glassy GeO_2 had formed.

1. Introduction

In many phases of solid state device preparation, thin films less than 100 Å in thickness are deposited on various substrates either as a built-in step in the production process or as an undesirable contamination on exposure to various ambient environments. The films which are due to contaminants are usually composed of either hydrous or anhydrous oxides carbonates, or nitrides of the bulk metal. Ellis [1] suggests the formation of a monoxide film on a germanium substrate after etching the sample in a solution of 48% HF:30% H_2O_2:H_2O_2(40:6:24) with no agitation. The film thicknesses were said to be of the order of 1670Å with a refractive index of approximately 1.8. The growth rates of the films reported were approximately 50 Å per second. Using attenuated total reflection, Beckmann [2] found that the thin films formed in a 40% HF:30% H_2O_2 (10:1) solution had an overall composition of $GeOH_2$.

The electrochemical behaviour of germanium in the aqueous solutions investigated by Turner [3] suggests that, after anodic treatment, a monolayer of hydroxyl ions is present on the surface of the germanium. With the combination of two holes (electrons) per germanium atom dissolving a mechanism is proposed whereby the germanium goes into solution as a complexion involving the hydroxyl (oxide) radicals. Cerniglia and Wang [4] studied Ge in H_2O_2 and reached a similar conclusion with respect to the role of the hydroxyl radical and the combination of the surface complex with holes. They proposed that the following two-step mechanism takes place during the dissolution process:

$$2H_2O_2 \rightarrow H_3O_2 + O_2H^- \quad (1)$$

$$Ge + O_2H^- + H_2O + 2e^+ \rightarrow \underset{\text{(surface)}}{Ge(OH)_2^{++}} + OH^- \quad (2)$$

Since in an aqueous solution holes can be supplied by the reaction between H^+ ions and H_2O_2 as presented below,

$$H_2O_2 + 2H^+ \rightarrow 2H_2O + 2e^+ \quad (3)$$

there would be an abundant supply of holes, and therefore this process would not be a rate determining step. The availability of holes in the

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germanium crystal would supplement this supply. The diffusion of holes from either the solution or from the bulk crystal then allows the formation of the final dissolution products in a solution of low pH:

$$\underset{\text{(surface)}}{Ge(OH)_2^{++}} + H_2O \rightarrow H_2GeO_3(aq) + 2H^+ \quad (4)$$

Johnson [5] suggests that the stable form of germanium in acid solutions is H_2GeO_3, metagermanic acid. Gmelin [6] lists the following reactions for germanium and germanium dioxide in aqueous solutions:

$$Ge + 5OH^- \rightleftarrows HGeO_3^- + 2H_2O + 4e^- \quad (5)$$

$$Ge + 3H_2O \rightleftarrows H_2GeO_3 + 4H^+ + 4e^- \quad (6)$$

$$Ge^{2+} + 2H_2O \rightleftarrows GeO_2 + 4H^+ + 2e^- \quad (7)$$

$$GeO_2 + H_2O \rightleftarrows H_2GeO_3 \quad (8)$$

This indicates that the most probable reaction product in aqueous solution would be metagermanic acid.

If, as suggested by Ellis [1], the germanium is first transformed to the divalent state, then as reaction (7) shows one would still expect the formation of GeO_2 and subsequent dissolution to metagermanic acid. Beckman [7] has studied the formation of oxide films on germanium anodes in alkaline electrolytes. However, there appears to be no direct evidence to indicate the chemical composition and thickness of any thin films formed on the surface of germanium in various solvents under standard chemical etching conditions.

Until recently the ellipsometric technique for studying the oxidation kinetics of semiconductor and metals and the characterisation of surface films, was hampered by the practical solution of the various equations involved in ellipsometry [8], and hence it has been customary to resort to various approximations. But Saxena [9] has shown that all of these approximations often lead to erroneous results even though the film thickness may be very small. However, in recent years the use of modern computers has allowed numerical solutions of the ellipsometric equations in their exact forms. The ellipsometric technique that is used most frequently to determine the refractive index n_1 and the thickness d_1 of a nonabsorbing thin film on an absorbing substrate requires accurate values for the optical constants of the substrate [10].

In this paper we will describe the use of ellipsometric methods to determine the refractive indices and the thicknesses of the thin films that form on cleaved germanium substrates in air, water, hydrogen peroxide and after washing with a hydrofluoric acid solution.

2. Description of Method

The experimental details of the ellipsometric method for measuring the refractive indices and the thicknesses of nonabsorbing thin films on absorbing substrates when in air, as well as when immersed in a liquid, has already been described in detail by Vedam *et al* [11, 12]; hence only a brief description will be given below. In general, if plane polarised light is incident upon a clean, highly polished absorbing substrate at some arbitrary angle, the reflected light will be elliptically polarised. The measured ellipticity parameters (Δ and ψ) will be different if a thin nonabsorbing film is present on the surface. In general, the parameters Δ and ψ depend on the values of n_2, k_2, n_1, d_1, the angle of incidence ϕ, and the wavelength λ, where n_2, k_2 are the optical constants of the substrate. If the value for the refractive index of the film is known, then the thickness of the films can be determined accurately [13], assuming that n_2, k_2 are accurately known. If the refractive index of the film is uncertain, then various refinement techniques [11] must be employed. We used the recently determined [14] values of the optical constants of germanium in the present studies and they have the values $n_2 = 5.46 \pm 0.10$ and $k_2 = 1.75 \pm 0.14$ for $\lambda = 5461$ Å.

The measurements were carried out at room temperature (22°C) with a Gaertner model L119 ellipsometer using a 5461 Å Hg arc light source at an angle of incidence ϕ of 70.9°. The ellipsometer was modified for the present experiment by the same type of liquid cell discussed earlier [11]. The cell was designed so that the light enters and leaves the cell normal to the cell windows. The cell was then lined with a cement that was chemically inert to water, hydrogen peroxide, and hydro-fluoric acid. The sample holder was a goniometer head which was supported from above, independent of the ellipsometer table. This permitted alignment of the sample in the light path, and removal of the solutions without disturbing the alignment.

3. Sample Preparation

Vedam, Knausenberger and Lukes [12] in their investigations on silicon found that the surfaces

TABLE I Ellipsometric data

Parameters determined	Natural film in air	Film after 1 h in H_2O	Film 5 min-4 h 30% H_2O_2	Film after drying 1 day in air
Δ	141.51	127.13	140.26	143.99
ψ	22.32	17.56	15.11	22.19
n_2*	5.46 ± 0.10	5.46 ± 0.10	5.46 ± 0.10	5.46 ± 0.10
k_2*	1.75 ± 0.14	1.75 ± 0.14	1.75 ± 0.14	1.75 ± 0.14
n_1	1.63 ± 0.01	1.63 ± 0.02	1.74 ± 0.02	1.63 ± 0.01
d_1(Å)	69	94	18	56
n_0	1.00	1.33	1.354	1.00

*Knausenberger and Vedam [13]

which were chemically polished were not representative of the undamaged material. The Δ and ψ measured on etched surfaces were approximately 2% lower than those observed on cleaved samples Therefore cleaved surfaces were used in the present work.

The 40 ohm-cm germanium samples used in this study were supplied by Sylvania Electric Company, Towanda, Pennsylvania. Chemical analysis showed that there was less than 1 ppb cation impurity content. The samples were cleaved parallel to the (1 1 1) surface by the Gobeli-Allen techniques [15].

The resulting cleaved surfaces were optically flat.

4. Discussion of Ellipsometric Results

Several measurements on the films that formed on such freshly cleaved surfaces after exposure to air gave a refractive index of 1.63 and a thickness of approximately 70 Å as shown in table I. These values agree with those observed by Knausenberger and Vedam for glassy GeO_2 thin films [14].

The value of 70 Å is representative of the film thickness on a sample that has been exposed for four days in air at room temperature. This thickness is relatively constant then over a period of several months [15].

In order to observe the reactivity of germanium and glassy germanium dioxide in deionised water, measurements of Δ and ψ were made after 1 h to allow a steady state to be established. No discolouration, gas evolution or any other change was visible on the surface. The index of refraction of the film was found to be 1.63, again that of amorphous GeO_2. However, the thickness of the film had increased slightly to approximately 95 Å. This increase would be expected on the basis of reaction (7) mentioned earlier. Although little is known about the kinetics of this reaction, on the basis of the increase in film thickness observed the reaction appears to be faster than the competing reaction (8) of the dissolution process to metagermanic acid. The very slight solubility of glassy GeO_2 in water has also been noted by Dennis and Laubengayer [17].

The water was then replaced in the cell by an aqueous solution of 30% hydrogen peroxide; the refractive index of which was 1.354. Initially there was considerable gas evolution; however, after approximately 5 min, the vigorous evolution subsided permitting measurement. The evolution of gas continued at a slow rate through the immersion. The solution was not stirred during the measurements. The variation of temperature was less than 1 to 2°C. The refractive index of the film changed to approximately 1.74, while the film thickness decreased to 18 Å. After 4 h, Δ and ψ has not changed significantly and were within experimental error. This indicates that the system had rapidly attained an equilibrium state with respect to the processes of film formation and dissolution. The continuous evolution of the gas means that the dissolution processes were not interrupted. The vigorous evolution initially suggests that the glassy GeO_2 film that formed in air and water was destroyed by the effect of the strong oxidising agent and that the mechanical processes were involved with escaping bubbles of hydrogen gas evolved in the oxidation processes.

After removal from the hydrogen peroxide solution, the sample was allowed to dry in air for one day. The refractive index of the film returned to the value of glassy GeO_2, with a slight increase in thickness. If the film formed in the hydrogen peroxide was stable, one would expect the refractive index to remain at approximately 1.74; variation might be expected due to the loss of water or gases trapped in the film during its formation. However, the change of the index of refraction to that of the glassy form, which is stable in air, indicates that the film formed in

H_2O_2 is probably stable only in aqueous peroxide solutions. This type of behaviour can be expected for a mixed film composed of $Ge(OH)_2$ at the surface, and a thick envelope of H_2GeO_3 about the sample. The apparent thickness of the film about the surface is attributed to a real film composed primarily of $Ge(OH)_2^{2+}$, and a heavy reaction envelope of metagermanic acid.

It should be mentioned here that the standard deviations of 0.01 to 0.03 in the values of n_1 were obtained from the present set of experimental data on Δ, ψ on eight different samples, and by using the published value of n_2 as 5.46 and k_2 as 1.75. Since these published values of n_2 and k_2 themselves have reported standard deviations of 0.10 and 0.14 respectively, the influence of this uncertainty in n_2 and k_2 in the final values of n_1 and d_1 was investigated, with the help of the computer program of McCrackin [18].

The mean values of n_1 and d_1 obtained for the range of possible values so evaluated are indicated as $\bar{n}_1$ and $\bar{d}_1$ in table II. The mean deviation $= \sum|X_i - X|/N_i$, as well as the maximum deviation from these mean values $\bar{n}_1$ and $\bar{d}_1$ are also entered in the same table. Here N_i indicates the total number of possible combinations of n_2, k_2, n_1 and d_1 satisfying the observed Δ and ψ, X and X_i are respectively the mean value and a possible value of n_1 or d_1 as the case may be.

It is seen that in every case, the mean values $\bar{n}_1$ and $\bar{d}_1$ agree with the values of n_1 and d_1 well within the estimated standard deviations. Further, the trend of the values is not altered in any manner, even if we take into consideration the mean deviations introduced due to uncertainties in the values of n_2 and k_2. Only when we take the extremely pessimistic view that the values are dominated by the maximum possible deviation reported in table II in each case, it is not possible to infer any meaningful data from the present study. Due to the number of observations made (eighty), it is felt that such a pessimistic approach is not warranted and that the values given in table I are considered reasonably valid.

Since metagermanic acid has not been isolated as a stable compound, its refractive index has never been reported. A search was then made for a compound similar in structure to that of H_2GeO_3 for an estimate of the refractive index.

Lithium metagermanate should be similar to the expected H_2GeO_3 structure. It is built of infinite chains of germanate tetrahedra. Due to the size of the lithium atoms with respect to the hydrogen and its physical similarities, this appeared to be a reasonable choice. Since the density of the material would be nearly the same, we would expect the refractive index of Li_2GeO_3 to also be nearly the same as that of H_2GeO_3. Schwartz [19] reports the refractive index of $\beta = 1.73$ for Li_2GeO_3. (The values of the refractive indices α and γ are not yet reported in the literature.) In contrast, the refractive indices reported for other forms of germanium dioxide are: $n_\omega = 1.695$ and $n_\epsilon = 1.735$ for the hexagonal α-quartz form, and $n_\omega = 1.99$ and $n_\epsilon = 2.05$ to 2.10 for the tetragonal rutile form [20].

The refractive index of Li_2GeO_3 agrees within experimental error with that of 1.74 measured for the thin films formed on the germanium in 30% H_2O_2, further supporting the formation of H_2GeO_3 in a reaction envelope.

A standard technique for removing surface contamination due to adverse chemical reactions is to rinse the germanium surface with a 48% solution of hydrofluoric acid. This presumably removes any oxides present, leaving a supposedly "clean" surface for device fabrication. The refractive index and thickness of the glassy GeO_2 film was first measured on a sample that had been immersed in water for several hours. The water was then removed from the cell, and the sample was washed in a stream of 48% HF. The surface was air-dried, and Δ and ψ were measured 5 min after washing. The film that was present was found to have the refractive index of glassy GeO_2; however, the thickness of the film was close to that expected for a freshly cleaved surface after 5 min exposure to air (50 Å). This

TABLE II Analysis of errors introduced by the uncertainties of the input data of optical constants of Ge

	Natural film in air	Film after 1 h in H_2O	Film 5 min-4 h 30% H_2O_2	Film after drying 1 day in air
$\bar{n}_1$	1.63	1.63	1.76	1.65
Mean deviation of $\bar{n}_1$	± 0.06	± 0.04	± 0.05	± 0.07
Max deviation from $\bar{n}_1$	± 0.10	± 0.06	± 0.06	± 0.08
$\bar{d}_1$	71	79	18	58
Mean deviation of $\bar{d}_1$	± 4	± 8	± 4	± 3
Max. deviation from $\bar{d}_1$	± 9	± 14	± 7	± 7

indicates that the oxide layer was indeed stripped by the HF solution; however, the natural glassy GeO_2 film began to develop almost immediately.

5. Conclusions

These results of the ellipsometric investigations suggest that the thin films that form on cleaved germanium surfaces in air and water have a refractive index of 1.63 which nearly matches that of glassy GeO_2. In hydrogen peroxide a film forms with a refractive index of approximately 1.74, with an apparent steady state thickness of approximately 18 Å. This film is attributed to a heavy reaction envelope produced by the surface reaction:

$$Ge + O_2H^- + H_2O + 2e^+ \rightleftarrows \underset{\text{(surface)}}{Ge(OH)_2^{2+}} + OH^- \qquad (9)$$

This reaction is probably controlled by a diffusion process of the O_2H^- species to the surface. With the diffusion of holes to the dissolving $Ge(OH)_2^{2+}$ complex, the final reaction

$$\underset{\text{(surface)}}{Ge(OH)_2^{2+}} + H_2O \rightleftarrows H_2GeO_3(aq) + 2H^+ \qquad (10)$$

It is suggested that the reaction products produce a layer of hydroxyl complexes [$Ge(OH)_2^{2+}$] adsorbed at the metal-film interface, and free $Ge(OH)_2$ and H_2GeO_3 (aq) forming a thick reaction envelope between the $Ge(OH)_2^{2+}$ surface layer and the solution. Upon drying, the refractive index of the film is again that of glassy GeO_2. This indicates that the film that forms in 30% H_2O_2 is a metastable one with respect to air. After rinsing the sample in HF, the oxide removed in the process was replaced immediately by the natural air film.

The ellipsometric technique has proven to be a useful tool for *in situ* investigation of the deposition and reactivity of thin films on metals and semiconductors.

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