

Optical band gap dependence on the oxalic acid concentration of antimony anodic oxide films

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A decrease of the optical band gap of thin films of anodized antimony was observed when the concentration of the oxalic acid used as an electrolyte was increased. The thin films of antimony were obtained using vacuum-thermal evaporation on glass substrates. Electrodes were attached to them and the samples were galvanostatically anodized at a constant temperature in a standard two-electrode cell in an aqueous solution of oxalic acid at various concentrations. The normal-incident transmittance and reflectance spectra of the samples were measured and used to calculate by different numerical methods the absorption coefficients and the optical band gaps.

Key words: anodized antimony, oxalic acid, optical band gap, Tauc plot

INTRODUCTION

Interest in the thin antimony oxide layers is mainly related to their use in batteries, corrosion protection and the creation of catalysts. The anodizing is a very simple and cheap process used to obtain thin oxide films. Layers of various metals and semiconductors in which a high voltage anodizing can be achieved were investigated over many years. Antimony is such a valve metal, which in anodizing shows interesting features such as the presence of induction periods of time when in galvanostatic mode the voltage remains stable for a long period of time, and then suddenly begins to grow as normal. The study [1] of this phenomenon shows dependence on the electrolyte concentration and has no generally accepted explanation yet. The aim of our experiment is to find if another physical property - the optical band gap depends on the concentration too. Such dependence is interesting from theoretical and practical point of view.

An effect of reducing the width of the band gap of anodically grown ZnO thin films by increasing the concentration of oxalic acid has been observed in [2]. The same phenomena of band gap structure modification of amorphous anodic Al oxide film by Ti-alloying is observed in [3].

EXPERIMENTAL

Anodized antimony films, the objects of this

study, were prepared in two stages. First, on borosilicate glass plates, thin layers of antimony were obtained by thermal evaporation in vacuum, situated to get gradually changing thickness. At the second stage a copper wire was attached to the film surface and the samples were placed in a galvanic bath at a constant room temperature. In a galvanostatic mode they were anodized using, at different concentrations, water solutions of oxalic acid as electrolyte. It is not possible to prepare a continuous, unbroken antimony oxide film if the thickness of the metallic antimony layer is constant. In this case cracks appear which can stop the process of anodizing on the parts of the film. The variable thickness of the antimony film provides a possibility for fully and smoothest oxidation of the layer, starting from the end with a smaller thickness and spread to the other end.

Measurements and calculations

X-ray diffraction studies show that the anodized layers have an amorphous structure. The thickness of the film on each sample was measured by interferometric method and used in calculations. All thicknesses are in the range of 200 – 340 nm.

In order to determine the optical band gap the spectrophotometer JASCO V-600 was used and the coefficients of transmission T and reflectance R were measured, illuminating the samples by incident light with different wavelengths, nearly normal to the surface. The optical band gap E_g can be extracted from the dependence of the absorption

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coefficient α on the light energy, which for amorphous materials is [4]:

$$(\alpha E)^{1/2} \approx E - E_g$$

E_g can be found approximating $(\alpha E)^{1/2}$ by straight line in the absorption region (Fig. 1 and Fig. 2).

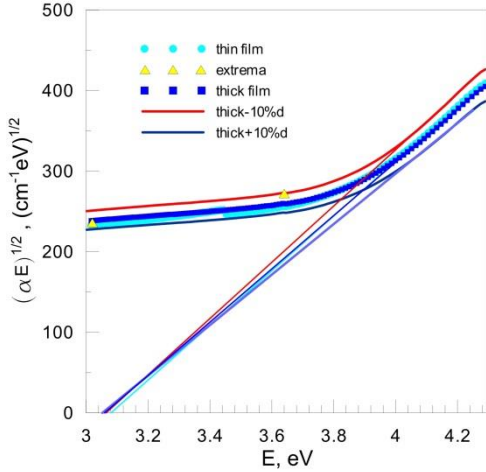


Fig. 1. Tauc plot for 0.01 M oxalic acid concentration.

The results shown by circles are calculated from expressions for thin film, the boxes are from formulae for thick film, triangles correspond to results obtained from extrema of R and T .

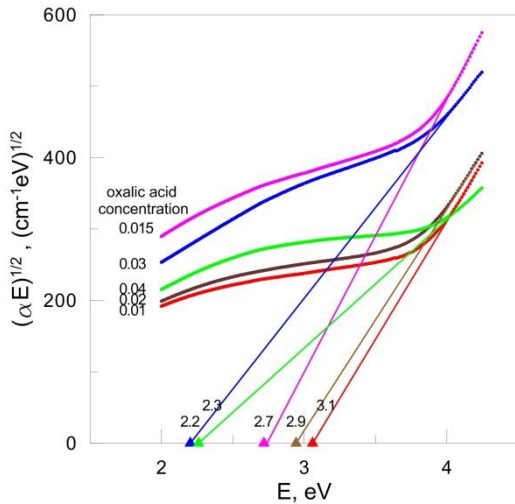


Fig. 2. Tauc plots for all oxalic acid concentrations. The tangent straight lines are used to find the optical energy bands shown at the bottom axis.

According to this method the absorption coefficient α have to be calculated from measured transmission coefficient T and reflectance coefficient R . They depend on the refractive indexes of the film and substrate, their absorption coefficients and the film thickness, according

expressions (1) – (2) given in Appendix. This system of two equations with two unknowns can be solved numerically for each wavelength, but a problem exists due to the periodic functions in Eqns. (1) and (2), which results in many solutions for the refractive index n . To select one an additional criterion is needed. We used n , calculated from the extreme of R and T according Eqn. (4) in Appendix and approximated linear in the regions between two extreme. The closest numerical solution is taken and referred in Fig. 1 as thin film.

We are interested of the region above 3.5 eV (Fig. 1), where the effects of interference are suppressed by the absorption. In the case of no coherent interference which happens in thick films, T and R are given by Eqns. (5) in Appendix. They are simpler than Eqns. (1) – (2) and have this advantage that can be solved explicitly – Eqns. (6) in Appendix. The results obtained, using this method, are referred in Fig. 1 as thick film.

We calculated absorption coefficients for all our samples using both methods. An example for a sample at 0.01M concentration is shown in Fig. 1. Dots denoted by circles are obtained from expressions for thin film Eqns. (1) – (2), the boxes are from Eqns. (6) for thick film and triangles correspond to results calculated from extrema of R and T . The difference between absorption coefficients obtained by both methods is small and the difference between correspondent optical band gaps does not exceed 0.06 eV for all samples. We calculated R and T according different models for the refractive index and extinction coefficient, including those in [5], and in all cases we found negligible the difference for the absorption coefficient in the absorption region.

Transmission and reflectance coefficients spectra for each sample are obtained in two separate measurements. It is possible that light rays from the spectrophotometer have been passed through different regions of the sample with different thickness. In order to explore the influence of this effect on the final results we calculated the absorption coefficient under assumption that transmission coefficient has a measured thickness, but the reflectance coefficient has a thickness which differs at $\pm 10\%$. The Eqns. (6) for thick film were modified and Eqns. (7) obtained were solved numerically as explained in Appendix. The correspondent results for one sample are shown in Fig. 1 by solid lines. The error due to different width is less than 0.02 eV in all cases.

RESULTS

The Tauc plot for samples anodized in oxalic acid with different concentrations is shown in Fig. 2. The absorption coefficients are calculated using Eqns. (6) for thick film. The corresponding concentration is shown at the beginning of each curve. The line tangent to the curve in the region of absorption intercepts the abscissa at the optical band gap E_g . Each point is denoted by triangle in Fig. 2 and the corresponding value for band gap is given.

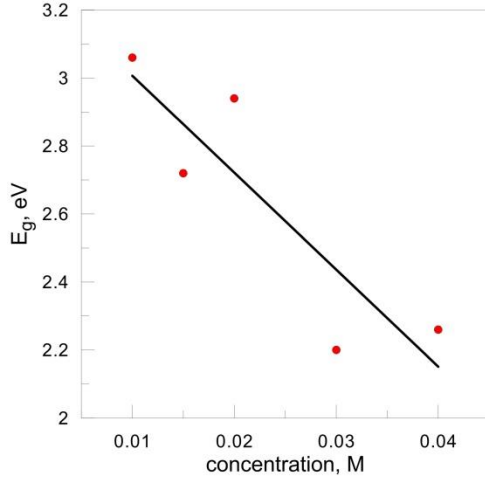


Fig. 3. Optical band gap of anodized antimony films depending on the concentration of the oxalic acid.

Fig. 3 shows the dependence of the optical band gap of anodized antimony thin films on the oxalic acid concentration. The straight line in Fig. 3 is a fit to the data. It is seen the variation of the molar concentration of the electrolyte has a significant effect on the optical band gap of the antimony films obtained in the process of anodic oxidation. The increase of the concentration leads to decrease of the band gap.

Our result corresponds to the reducing of the band gap of anodic oxid film of other metals. Such a decrease of the band gap due to increase of the concentration of oxalic acid has been observed in [2], but for ZnO thin films. This effect is explained there by the structure of the layer, composed of nanocrystals. The observed dependence correlates with the increasing size of the nanocrystals with concentration. Our case is different because the anodized antimony film has an amorphous structure. In [3] is observed the decrease of the band gap energy of Ti-alloyed anodic Al oxide with increasing Ti concentration.

CONCLUSIONS

Thin films of anodized antimony in solution of oxalic acid at various concentrations were obtained.

Their optical band gaps were calculated using very simple methods, based on the measurements of the coefficients of transmission and reflectance. A strong dependence of the optical band gap on the oxalic acid concentration has been observed.

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APPENDIX

For a thin film on a thick transparent layer the transmission coefficient T for light normal to the surface is given by [5]:

$$T = \frac{Ax}{B - Cx - Dx^2}$$

$$A = 16s(n^2 + k^2)$$

$$B = [(n+1)^2 + k^2][(n+1)(n+s^2) + k^2]$$

$$C = [(n^2 - 1 + k^2)(n^2 - s^2 + k^2) - 2k^2(s^2 + 1)]2 \cos \phi$$

$$- k[2(n^2 - s^2 + k^2) + (s^2 + 1)(n^2 - 1 + k^2)]2 \sin \phi$$

$$D = [(n-1)^2 + k^2][(n-1)(n-s^2) + k^2] \quad (1)$$

where n is the refractive index and k is the extinction coefficient of the film, s is the substrate refractive index and:

$$\phi = 4\pi nd / \lambda, \quad x = \exp(-\alpha d), \quad \alpha = 4\pi k / \lambda \quad (2)$$

According to [6] the reflectance R from a thin film on a thick substrate illuminated at nearly normal incident light is given by:

$$R = \frac{A + Bx + Cx^2}{D + Ex + Fx^2}$$

$$A = [(n-1)^2 + k^2][(n+s)^2 + (k+k_s)^2]$$

$$C = [(n+1)^2 + k^2][(n-s)^2 + (k-k_s)^2]$$

$$D = [(n+1)^2 + k^2][(n+s)^2 + (k+k_s)^2]$$

$$\begin{aligned}
F &= [(n-1)^2 + k^2] [(n-s)^2 + (k-k_s)^2] \\
A' &= (1-n^2 - k^2)(n^2 - s^2 + k^2 - k_s^2) + 4k(nk_s - sk) \\
B' &= 2(1-n^2 - k^2)(nk_s - sk) - 2k(n^2 - s^2 + k^2 - k_s^2) \\
B &= 2[A' \cos \phi + B' \sin \phi] \\
C' &= (1-n^2 - k^2)(n^2 - s^2 + k^2 - k_s^2) - 4k(nk_s - sk) \\
D' &= 2(1-n^2 - k^2)(nk_s - sk) + 2k(n^2 - s^2 + k^2 - k_s^2) \\
E &= 2[C' \cos \phi + D' \sin \phi] \quad (3)
\end{aligned}$$

where n, k, s, x, α, ϕ have the same meaning and k_s is the substrate extinction.

The condition for extreme of T and R is:

$$2nd = m\lambda \quad (4)$$

where $m=1,2,3\dots$ is an integer number in the case of maximum of T and minimum of R , and a half-integer number $1/2, 3/2, 5/2\dots$ in the case of minimum of T and maximum of R . It is seen the refractive index can be easily calculated if the thickness d is known and the order m of at least one extremum is known.

The formulae of transmittance and reflectance from a thick slab given in [4] are:

$$\begin{aligned}
R &= R_0 \left[1 + \frac{(1+R)^2 \left(1 + \frac{k^2}{n^2} \right) e^{-2cad}}{1 - R_0^2 e^{-2cad}} \right], \\
T &= \frac{(1-R_0)^2 e^{-cad}}{1 - R_0^2 e^{-2cad}} \left(1 + \frac{k^2}{n^2} \right) \\
R_0 &= \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (5)
\end{aligned}$$

In our case $k/n \ll 1$, and Eqns. (5) can be rewritten:

$$R = R_0 \frac{1 + (1-2R_0)x^2}{1 - R_0^2 x^2}, \quad T = \frac{(1-R_0)^2 x}{1 - R_0^2 x^2}$$

These equations can be solved explicitly:

$$\begin{aligned}
R_0 &= \frac{1 + 2R - R^2 + T^2 - \sqrt{(1-2R+R^2-T^2)^2 + 4T^2}}{2(2-R)} \\
x &= \frac{-1 + 2R - R^2 + T^2 + \sqrt{(1-2R+R^2-T^2)^2 + 4T^2}}{2T} \quad (6)
\end{aligned}$$

The absorption coefficient is calculated from (2), and after that k and n :

$$n = \frac{1 + R_0 + \sqrt{4R_0 - k^2(1-R_0)^2}}{1 - R_0}$$

If R and T of a sample are measured at different thickness the formulae above must be changed. Let us suppose that R is measured at thickness d_1 and T at d_2 :

$$\begin{aligned}
x_1 &= \exp(-\alpha d_1), \quad x_2 = \exp(-\alpha d_2), \\
R &= R_0 \frac{1 + (1-2R_0)x_1^2}{1 - R_0^2 x_1^2}, \quad T = \frac{(1-R_0)^2 x_2}{1 - R_0^2 x_2^2} \quad (7)
\end{aligned}$$

These equations can be solved very easily by iteration method. Starting with the values obtained at equal thickness, R_0 from the first equation is found and after that α from the second. The convergence is very fast and 2-3 iterations are enough.

ЗАВИСИМОСТ НА ОПТИЧЕСКАТА ШИРОЧИНА НА ЗАБРАНЕНАТА ЗОНА НА АНОДИРАНИ АНТИМОНОВИ ФИЛМИ ОТ КОНЦЕНТРАЦИЯТА НА ОКСАЛОВАТА КИСЕЛИНА

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(Резюме)

Наблюдавано е намаляване на оптичката широчина на забранената зона на тънки слоеве от анодиран антимион, когато концентрацията на оксаловата киселина използвана като електролит се увеличава. Тънките слоеве от антимион бяха получени чрез вакуумно-термично изпарение върху стъкло. Към тях бяха прикрепени електроди и бяха анодирани галваностатично при постоянна температура в стандартна дву-електродна клетка във воден разтвор на оксалова киселина с различни концентрации. Спектрите на преминаване и отражение, перпендикулярно на повърхността на пробите, бяха измерени и използвани за пресмятане чрез различни числени методи на коефициентите на поглъщане и широчините на забранените зони.