Charge transport in gap structures based on amorphous Al$_2$O$_3$

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Abstract. The charge transport in amorphous layers of oxide of aluminum Al$_2$O$_3$ in the temperature range $T=223$-273K is studied. It was found the existence of hopping conduction mechanism in studied layers. The values of dispersion parameter $s$ and activation energy $E_A$ are determined.

1. Introduction

Aluminium oxide possesses a number of interesting physical and chemical properties - high melting point, heat conductivity and the dielectric parameters, increased radiation stability, high electrical specifications, wide band-gap, minor external impact resistance, shows no chemical reaction at contacted materials, thus causes its wide application as an active element in modern microtronics and electrooptics. During the recent years films of aluminium oxide have been analyzed as a dielectric layer in capacitor structures. Thanks to high dielectric capacitance amorphous films of Al$_2$O$_3$ are considered as one of alternatives of replacement of silicon oxide in the process of formation of superfine gate dielectric layers in technology of metal-oxide-semiconductor structure [1].

Bulk conduction of amorphous aluminium oxide layers was investigated by authors [2], [3]. The existence of several conduction mechanisms was discovered: from migration of weakly bound metal ions to hopping charge transport of over localized states near the Fermi level [2]. It is found that conduction of Al$_2$O$_3$ in the temperature range 223 K < $T$ < 373 K is predominantly based on electron jump and is adequately described by equation [4]:

$$\sigma(\omega) = \frac{\pi^2}{96} N_F^2(E_F) k T a n^4 \nu_{ph} e^2,$$

where $e$ – is electron charge; $k$ – Boltzmann constant; $N_F$ – density of states near the Fermi level; $a = 1/\alpha$ – localization radius; $\alpha$ – decay constant of the localized charge carrier wavefunction $\psi \sim e^{-\alpha r}$; $\nu_{ph}$ – phonon frequency.

The aim of this work was establishment of regularities of processes of charge transport in gap structures based on amorphous Al$_2$O$_3$, obtained by method atomic layer deposition (ALD).

2. Experimental details

The aluminium oxide layers in gap structures Al-Al$_2$O$_3$-Al were obtained by method ALD on $p$-type silicon Si (100) surface-supported substrate with its resistivity of $\rho = 10$ Ohm • cm. Drawing layers was carried out at a temperature of 300 K in the atmosphere of trimethylaluminum Al
(CH$_3$)$_3$ (TMA) with use of solution of nitric acid (HNO$_3$) and water as reagents. Aluminum contact points in area of 0.24 mm$^2$ were applied by thermal evaporation method. The thickness of oxide layers was 100 nm.

Measurement of surface conductivity was conducted in frequency range 10$^{-1}$…10$^6$ Hz and in the temperature range 223 K…273 K with spectrometer “Concept 81” (Novocontrol Technologies GmbH). System consist of frequency impedance analyzer ALPHA ANB, flow cell, temperature control system Novocool Cryosystem, Dewar flack containing vapor and feed control of nitrogen gas, and also automatic data collecting system with computer interface. The temperature stabilized with accuracy $\approx$ 0.5 $^\circ$C, experimental uncertainty error exceed 1.0 %. The complex conductivity $\sigma^*$ was calculated from the complex impedance $Z^*$ by equation:

$$\sigma^* = \sigma' - i\sigma'' = \frac{-i S}{\omega Z^*(\omega) d}.$$  

3. Results and discussion

There is frequency dependence of the electrical conductivity $\sigma'$ in different temperature range in Figure 1. The figure shows that the conductivity of investigated sample depend on temperature and increases with frequency increase of external variable field. There are two regions of $\sigma'$ frequency dependence: low and medium frequency. There was discovered exponential dependence of electrical conductivity from frequency in the region of low frequency according to the law $\sigma' \sim \omega^s$. Exponent $s < 1$ steadily decreases with temperature in the range of (0.75 ± 0.01) to (0.50 ± 0.01). The temperature dependence of $\sigma'$ has exponential character (figure 2), with activation energy $E_a = (0.21 ± 0.01)$ eV. It is well-known that the conductivity of band type is generally frequency-independent up to 10$^{10}$ – 10$^{11}$ Hz. Discovered dependencies reveal that charge transport occurs by electron jump between localized states in band-gap. The probability of jumps and their number increases with the increase of temperature and frequency, simultaneously delocalization of carriers within state groups occurs that is accompanied by decrease of coefficient $s$. Probably the role of localized states execute generally fluctuations of the substance density in layers of Al$_2$O$_3$ due to its disordered structure [5]. Increasing filling of such states with the rise of temperature leads not only to delocalization of the carriers but also to increase in conductivity.

![Figure 1](image-url)
Figure 2. Temperature dependence of real conductivity in gap structures on the basis of aluminium oxide.

By the shape of I-V characteristic (Figure 3) that was measured at room temperature it can be concluded that in these films the conductivity mechanism is monopolar (electronic) [6]. The process of charge transport in amorphous aluminium oxide is considered on the basis of monopolar injection when charges of one type are introduced in dielectric material, in this context this is electronic monopolar conduction. It is assumed that charges are introduced from the side of aluminium electrode.

Figure 3. I-V characteristic of planar structures on the basis of amorphous aluminium oxide.

The samples of two types were investigated for discovery of reagent efficiency when amorphous aluminium oxide layers are synthesizing: No1 were used trimethylaluminium $Al(CH_3)_3$ (TMA) and water vapor, No2 were used TMA and nitric acid, sample thickness was 100 nm.

The use of nitric acid solution as the reagent leads to increase of surface conductivity value (figure 4), that probably related to structural feature of amorphous aluminium oxide. The structure of examples (type No1) is characterized by its short-range order that is the same with arrangement of atoms in
crystal phase $\alpha-Al_2O_3$ (hexagonal structure) [7]. In examples of type No2 short-range order depends on arrangement of atoms in mixture phase $\gamma-Al_2O_3$ (triclinic structure) and small quantity of pseudoboehmite ($\gamma-AlOOH=10\%$) (triclinic structure) [8], in the other words the used reagent determines the parameters of structure.

Modification of structure conductivity with use of various reagents correlates with structural mechanisms of polarization by imposition to structures of ac potential using frequency as well as temperature factors. The frequency dependence of electrical module $M''$ at room temperature is shown in Figure 5. The value of the most probable relaxation time $\tau_{max}$ changes with the change of reagent.

4. Conclusions

Thus, it was found that layers conductivity of $Al_2O_3$ in the investigated frequency range is described with power law where the exponent of power is temperature-dependent. The charge transport in the samples under investigation occurs by jump mechanism in the band-gap via the localized states,
and it is thermally activated process with activation energy $E_a = (0.21 \pm 0.01)$ eV. The use of nitric acid solution as reagent in synthesis of $\text{Al}_2\text{O}_3$ layers leads to increase of surface conductivity value that is connected with structural features of amorphous aluminium oxide.

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5. References
[1] Wilk G D Wallace R M Anthony J M 2001 High-k gate dielectrics: Current status and materials properties considerations J. Appl. Phys. 89 p 5243
[2] Borisova T M Castro R A 2013 Mechanism of charge transport in Si/$\text{Al}_2\text{O}_3$/Al structures Journal of Physics: Conference Series 461 p 012017
[3] Novikov Yu N Vishnyakov A V Gritsenko V A Nasyrov K A 2010 Charge transport in aluminium oxide: phonon – assisted trap ionization Izvestia: Herzen University Journal of Humanities and Sciences 122 pp 46 - 52
[4] Pollak M 1971 Frequency dependence of conductivity in amorphous solids Phil. Mag. 23 pp 519 - 542
[5] Mott N F 1974 Electronic Processes in Non-Crystalline Materials (Mott N F Davis E Moscow Mir Publ 1) p 472
[6] Novikov Yu N Gritsenko V A Nasyrov K A 2009 The Manyfon mechanism of trapionization in $\text{Al}_2\text{O}_3$: experiment and numerical modeling Technic. Phys. Lett. 89 10 pp 599-602
[7] Choong-Ki Lee Eunae Cho Hyo-Sug Lee Kwang Soo Seol Seungwu Han 2007 Comparative study of electronic structures and dielectric properties of alumina polymorphs by first-principles methods Physical review. 76 p 245110 pp 1 - 7
[8] Yakovleva N M Anicai L Yakovlev A N Dima L Khanina E Ya Chupakhina E A 2003 Structure and Properties of Anodic Aluminum Oxide Films Produced in $\text{HNO}_3$ Solutions Inorganic Materials 39 1 pp 50 - 56