



Dielectric Properties of Al-Nb Amorphous Mixed Oxides

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An impedance study of amorphous thin oxide films grown on sputtered Al-Nb alloys is presented. The characterization of the electronic properties of mixed amorphous oxide on the basis of the theory of amorphous semiconductor Schottky barrier has been carried out for anodic film on Al-92at.%Nb in a very detailed manner. The semiconductor to insulator transition of formed oxides as a function of the alloy composition at fixed final voltage has been supported by differential admittance study. A possible rationale for this transition has been suggested taking into account the changes of solid state properties, optical bandgap and electronic structure of the films, derived from the fitting of the differential admittance curves at different frequencies.

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In order to satisfy the requirement of miniaturization in modern linear integrated circuits, electronic components are developing toward smaller volume. For electrolytic capacitors this issue can be achieved by increasing the specific capacitance, i. e. by increasing the dielectric constant and the roughness factor. Al_2O_3 is a wide bandgap, E_g , insulator¹ with an amphoteric character, widely employed as dielectric in electrolytic capacitors ($\epsilon \sim 9$). It can be directly grown on Al metal by anodizing, and an easy electrochemical etching process allows to increase the specific surface of this metal.

Nb_2O_5 is a n-type semiconductor with relatively lower bandgap ($E_g \sim 3.30 \pm 0.1$ eV)^{2,3} and chemically stable in a wide range of pH. A very high, field dependent, dielectric constant ($\epsilon \sim 53$)²⁻⁴ is reported for anodic niobia, which makes this oxide a very appealing high k material, even if the possibility to use Nb_2O_5 as dielectric is limited by its poor blocking character.

In Refs. 5–7 the use of chemically prepared Al_2O_3 Nb_2O_5 composite oxides is suggested as a viable route to increase the dielectric constant with respect to that of pure alumina. This effect is also observed for Al-Nb mixed oxides grown by anodizing sputter deposited Al-Nb alloys.⁸ An increase in the dielectric constant up to ~ 22 is reported for anodic films grown on Al-44at.%Nb, which was the Nb richest investigated alloy.

In a recent work⁹ we have shown how it is possible to tailor bandgap, flatband potential and behavior (n-type semiconductor or insulator) of Al Nb mixed oxides, prepared by anodizing sputtering deposited Al Nb alloys covering all the composition range between pure Al and Nb. In this work the effect of Al/Nb ratio in determining their dielectric and electronic properties was studied by means of both electrochemical impedance spectroscopy (EIS) and differential admittance (DA) measurements. The dependence of admittance components for the Nb richest investigated alloy will be discussed quantitatively on the basis of the amorphous Schottky barrier theory.

Experimental

Al Nb alloys were deposited by magnetron sputtering using an Atom Tech Ltd system, with targets of aluminum (99.999%) and niobium (99.9%). Sputtering was performed in 5×10^{-3} mbar argon after previous evacuation to 5×10^{-7} mbar. The substrates consisted of high purity aluminum sheet that had been electropolished for 180 s at 20 V in a solution of ethanol and perchloric acid (4:1 by vol.) at 283 K. Al, Nb and Al-Nb alloys, containing 9, 40, 55, 66, 81 and 92 at.% niobium have been obtained, according to Rutherford Back Scattering (RBS) analysis.^{8,9} Anodic films were grown potentiodynamically to 9 V vs. Ag/AgCl (silver/silver chloride; 0.198 V vs SHE) on all the investigated alloys at 100 mV s⁻¹ in 0.1 M ammonium baborate (ABE) (pH ~ 8.5), where both Al_2O_3 and Nb_2O_5 are

reported to be thermodynamically stable according to the Pourbaix's diagrams relative to Al H₂O and Nb H₂O at room temperature.¹⁰

Electrochemical impedance spectroscopy (EIS) data for anodized alloys were obtained using a Parstat 2263 (PAR), controlled by a computer via Electrochemistry PowerSuite software. A three-electrode arrangement was used, consisting of the anodized specimen, a reference electrode (silver/silver chloride) and a Pt net having a very high specific area, immersed in 0.2 M Na_2HPO_4 . The impedance spectra were generated by applying a sinusoidal signal of amplitude 10 mV over the frequency range 0.1 Hz–100 kHz. The resultant spectra were analyzed with Zview software.

Results and Discussion

In Fig. 1 we report the anodizing curve relating to Al 66at.%Nb. As typical of valve metals, after an initial increase the current density reaches an almost constant value which remains unchanged up to the selected final formation voltage; it is important to stress that the charge density increases linearly with the potential during the anodizing, while it remains constant during the reverse scan, according to the theory of high field growth mechanism for valve metals. As expected for anodic barrier oxides a very low current density is measured in the reverse scan, due the formation of a blocking film. From the overall charge circulating during the anodizing, and by assuming for the oxide density and molecular weight the values obtained by averaging the density, ρ , and molecular weight, MW, of the pure oxides, it was possible to roughly estimate the film thickness, as shown in Table I. An Al/Nb ratio into the oxide coincident with that of the base alloy was assumed in agreement with previous results reported in the literature, based on Rutherford Back Scattering analysis of the anodic film composition.^{8,9} The estimated values compare well with

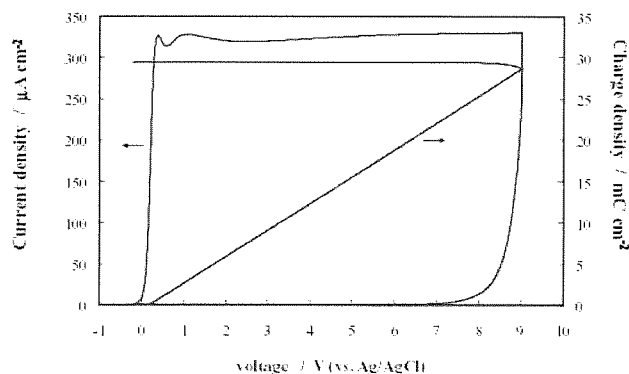


Figure 1. Current density and charge density vs potential curves recorded during the potentiodynamic anodizing of Al-66at.%Nb at 100 mV s⁻¹ in 0.1 M ABE.

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