

INFLUENCE OF MAGNETRON SPUTTERED TiN AND VN  
COATINGS ON THE ELECTRICAL IMPEDANCE OF  
ALUMINIUM ELECTRODES

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**Abstract**

In this work, TiN and VN coatings were applied on aluminium electrodes by direct current (DC) magnetron sputtering in order to study the influence of the protective coatings on the electrical impedance of the substrate. The structure of the samples was studied using X-ray diffraction (XRD). The microhardness of the substrate and the coated samples was also determined. The electrical impedance of the substrates with and without coatings was also studied and the results were used for evaluation of the applicability of such coatings for interface electrodes for flexible electronics. Electric impedance spectroscopy in a wide frequency range was applied for interlayer and surface contact properties determination. Results showed improved stability and conductivity of the electrodes coated using the TiN and VN thin films, particularly in the low frequency range.

**Key words:** TiN, VN, electrical impedance, aluminium electrodes, magnetron sputtered

**Introduction.** Aluminium and its alloys are highly applicable in electronics due to their excellent physical properties such as high mechanical strength, low

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electrical resistivity, high thermal conductivity, etc. However, electrical components, particularly those made of pure aluminium, tend to oxidize due to aluminium's high reactivity with the oxygen found in the surrounding air. There are a number of aluminium oxides that can be formed during this process, however, the most common one is the  $\text{Al}_2\text{O}_3$  phase [1]. The formation of oxide layers on the surface of the aluminium components protects the entire volume of the components from oxidizing. Aluminium oxides have been proven to have a vast application in the fields of electronics, due to their excellent properties as semiconductors [2]. However, when used in the field of electrical engineering, particularly integrated in electrical contact systems, the properties of Al as a pure metal are required, and the  $\text{Al}_2\text{O}_3$  passivating layers are regarded as isolators. This poses the need for modification of the surface of aluminium contacts in order to avoid the formation of oxide layers.

This could be achieved by applying surface coatings on the aluminium contacts. There are a number of techniques used for the formation of surface coatings such as electron-beam physical vapour deposition (EB-PVD), magnetron sputtering, chemical vapour deposition (CVD), and more. They all have their advantages and disadvantages, but in the present work reactive DC magnetron sputtering was used due to the higher energy of the ions compared to other methods, which leads to the in-depth integration of the coating in the structure of the samples, thus to the increase of the adhesion between the deposited particles and the substrate [3]. Furthermore, using DC magnetron sputtering it is easily possible to implement active gases in the vacuum chamber such as  $\text{O}_2$  and  $\text{N}_2$ , which react with the sputtered metallic ions and form chemical bonds. During this process, oxide-based and nitride-based compounds are formed and deposited atop the surface of the substrates. The newly formed compounds have unique properties depending on the sputtered metal during the process.

A highly popular choice both in research and industrial fields is the application of TiN and VN coatings in the form of protective layers. This is attributed to their excellent mechanical [4,5] and electrical properties [6,7], their superb corrosion resistance [8], and their high melting points [9,10]. Despite the extensive study on the structure and properties of TiN and VN their possible application in electrical contact systems has been poorly studied.

For this reason, in this work, TiN and VN coatings were applied on the surface of Al6082-T6 substrates and their influence on the electrical impedance of the substrates was studied.

**Experimental part.** TiN and VN were applied using reactive DC magnetron sputtering in an  $\text{Ar}/\text{N}_2$  environment on Al6082-T6 substrates with dimensions of  $12 \times 12 \times 3$  mm. The gas pressure was set to  $5 \times 10^{-3}$  Pa while depositing the TiN coating, and to  $2.4 \times 10^{-2}$  Pa while depositing the VN one. Apart from the different partial pressures the same technological conditions of layer deposition were used – a sputter power of 450 W, deposition time of 60 s, substrate temper-

ature of 300 °C, and a bias voltage of  $|-100\text{ V}|$ . In all cases before depositing the coatings cathode cleaning was employed in a vacuum environment to ensure the purity of the substrates' surface. A small underlayer of TiN with a thickness of about 100 nm was deposited on the substrates before depositing the VN layer in order to improve the adhesion between the VN coating and the substrates.

The thickness of the coatings was determined using an optical profilometer Zeta-20. The TiN coating has a thickness of 560 nm and the VN one has a thickness of 1008 nm taking into consideration the TiN underlayer.

The structure of the coatings was studied using X-ray diffraction experiments with a  $\text{CuK}\alpha$  radiation with a wavelength of 1.54 Å. The experiments were performed in a Bragg–Brentano mode using a Bragg angle in the range of 30–90 degrees. The detected phases were identified using the International Centre for Diffraction Data (ICDD) database by comparing the results to the ones included in the database for Al, TiN, and VN, corresponding to PDFs #040787, PDF #381420, and PDF #350768.

The Vickers hardness of the samples was also determined using a ZwickRoell Dura Scan 10/20 G5 microhardness tester at a maximum applied load of 1N, and a duration of each measurement of 10s. The experiments are in agreement with the following standard – ISO 6507-2.

The experimental setup for measuring the electrical conductivity consisted of an Agilent 4294A impedance analyser with an Agilent 16451B attachment. Information regarding the impedance of the samples was obtained using the parallel method with two electrodes. The method is illustrated in Fig. 1. The samples with and without coatings were placed between two parallel electrodes with a constant applied contact force of 5 N. The measured impedance corresponds to the resistance of the entire sample. In addition, an electric impedance spectroscopy in the range of 40 Hz to 1 MHz was employed in order to study the effect of the skin effect on the different samples.

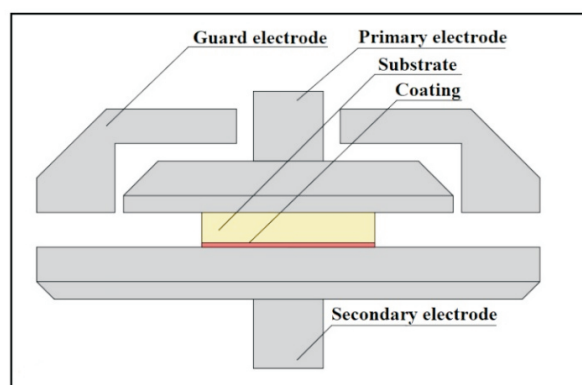


Fig. 1. Parallel method with two electrodes

**Results and discussion.** Figure 2 shows the results obtained during the X-ray diffraction experiments. The diffractograms were taken for both the TiN coated and the VN coated samples. In both cases a polycrystalline structure is observed consisting of an aluminium phase and a TiN, and a VN phase, corresponding to the different samples. The aluminium phase observed during the experiments is in the form of a face-centred cubic structure. The aluminium phase in the case of the Al/VN sample was detected at a  $2\theta$  angle of  $38.829^\circ$ ,  $45.079^\circ$ ,  $65.352^\circ$ ,  $78.535^\circ$ , and  $82.736^\circ$  corresponding to the following planes (111), (200), (220), and (311). The same orientations of the aluminium phase were also detected regarding the Al/TiN sample corresponding to the following Bragg angles –  $38.724^\circ$ ,  $44.974^\circ$ ,  $65.299^\circ$ ,  $78.429^\circ$ , and  $82.631^\circ$ . When comparing the Bragg angle of the detected peaks to the standard ones given in the ICDD database it is evident that all peaks in this work are offset in the positive direction. This signifies that a decrease of the interplanar spacing between the crystals, which in turn leads to a reduction of the lattice constant, has occurred. According to the theory of crystallographic analysis, this offset signifies to a decrease of the size of the aluminium crystallites as a function of the applied thermal treatment imposed by the necessary technological conditions for thin film deposition. Previous studies [11] indicate that a reversing of the heat treatment of aluminium alloys is possible at temperatures of  $200\text{--}350^\circ\text{C}$ . Subjecting heat-treated aluminium components to such high temperature environments results in reversing of the heat treatment process, and in turn resulting in the significant reduction of the alloy's mechanical properties. These results are in complete agreement with the results presented in

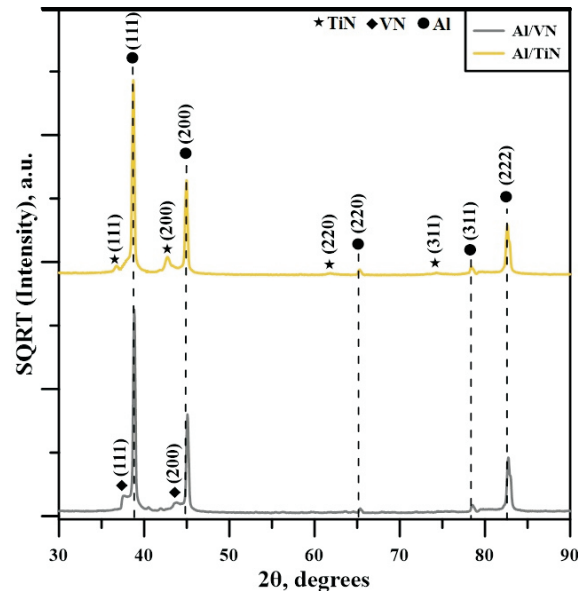


Fig. 2. X-ray diffractograms of the samples

the current work. Additionally, the bombardment of the substrate with energized particles also results in the formation of a thermal energy input proportional to the energy potential of the particles. This furthermore increases the temperature of the specimens during the deposition process.

Examining the results of the X-ray diffraction experiments the VN phase was detected at  $2\theta$  angles of  $37.463^\circ$  and  $43.530^\circ$  corresponding to the (111) and (200) planes. The TiN phase was also detected oriented towards the (111), (200), (220), and (311) planes corresponding to the  $36.728^\circ$ ,  $42.715^\circ$ ,  $61.885^\circ$ , and  $73.913^\circ$  Bragg angles. Evidently both the TiN and the VN phase experienced thermal expansion due to the high energy thermal environment formed during the layer deposition process, resulting in the increase of their lattice constants and thus the increase of the size of their crystallites. This explains the reorientation of the unit cells towards the  $\langle 111 \rangle$  family of planes as supposed to the  $\langle 100 \rangle$  one.

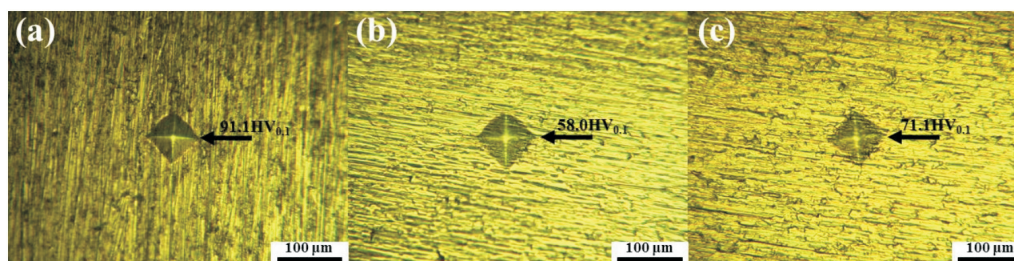


Fig. 3. Vickers hardness indentations of: (a) an untreated Al6082-T6 substrate; (b) Al6082-T6/VN specimen; (c) Al6082-T6/TiN specimen

In order to study the mechanical properties of the obtained samples their microhardness was studied. A polished, but otherwise untreated sample of Al6082-T6 was used as a control (Fig. 3a). The obtained Vickers hardness of that sample had an average value of  $91.1\text{HV}_{0.1} \pm 4.0\text{HV}_{0.1}$ . According to previous research [12] the standard Vickers hardness of Al6082-T6 is 95.0HV. The slight deviation off the standard value could be caused by the employed mechanical treatment required for the preparation of the sample before layer deposition. The microhardness of the coated samples was studied at their surface. Since the coatings' thicknesses are too low for such high indenter loads the obtained results do not indicate the microhardness of the coatings alone, but the summary of the coatings' and the substrates' hardness. The average microhardness obtained for the VN coated specimen was  $58.0\text{HV}_{0.1} \pm 1.8\text{HV}_{0.1}$  (Fig. 3b), and the one for the TiN coated specimen was  $71.1\text{HV}_{0.1} \pm 2.2\text{HV}_{0.1}$  (Fig. 3c). The authors of [11] discuss the influence of subsequent heat treatment on already heat-treated aluminium alloys. According to their research subsequent heating of heat-treated aluminium alloys leads to a significant worsening of the mechanical properties of the alloy. This means that preheating the substrates to  $300^\circ\text{C}$  has led to the worsening of the mechanical properties of the substrates, which is the reason for obtaining much

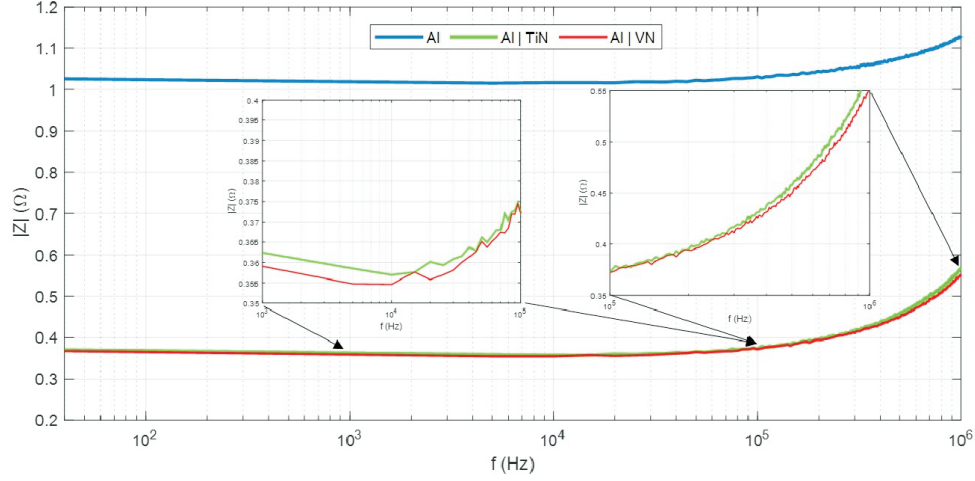


Fig. 4. Electrical impedance module of the pure aluminium samples and the ones coated with TiN and VN

lower microhardness values for the coated samples compared to the control. This is in agreement with the information given by the XRD analysis.

The results of the electrical impedance experiments are shown in Fig. 4. They indicate that the aluminium substrate exhibits very high electrical resistivity values, which is predominantly due to the formed oxide layer atop its surface. The electrical resistivity of aluminium is also very highly dependent of the applied heat treatments during the manufacturing process. This was also observed by LAPOVOK et al. [13] who demonstrated the influence of heat treatments on the electrical conductivity of aluminium single crystals and found that after a heat treatment of the aluminium crystal its electrical conductivity increased by 3.7%. This is attributed the thermal expansion of the aluminium crystal and thus the increase of its surface area. However, the substrate used in this work was a T6 heat-treated aluminium alloy. As previously discussed the applied heat during the deposition process led to the diminishing of the size of the crystallites and thus to the formation of a structure with a higher distance between the crystallites. This also leads to the reduction of the electrical conductivity of the control aluminium substrate. The impedance module of the control aluminium substrate reached values of  $1.03 \Omega$  at a frequency of 40 Hz and  $1.13 \Omega$  at 1 MHz. In comparison the impedance of the TiN and the VN coated samples was the same at low frequencies –  $0.368 \Omega$  at 40 Hz, and deviated slightly at higher frequencies being  $0.566 \Omega$  and  $0.551 \Omega$ , correspondingly, at 1 MHz.

During the experiments, a drop of the electrical impedance module was observed in all cases at a frequency of about 6 kHz. This was caused by the reactive capacitance of the samples themselves and the reactive capacitance formed be-

tween the two electrodes during the measurements. Evidently, in the case of the coated samples the impedance values dropped further than the ones for the pure sample at the same frequency. This is caused by the higher reactive capacitance of the coated samples. Due to the applied thin film on the surface of the substrate additional reactive capacitances form between the two coatings' planes and also in the boundary between the coatings and the substrate. This increases the influence of the capacitive component resulting in the reduction of the impedance at that frequency. However, due to the higher reactive capacitance of the coated samples the influence of the skin effect on them increased. The control aluminium samples' impedance increased by only 9% from the low to the high frequency range. In comparison, the TiN's impedance increased from 40 Hz to 1 MHz by 35%, and the same for the VN coating increased by 33%. The slightly lower increase of the impedance of the VN coating can probably be attributed to the different thickness of that coating compared to the TiN one. Evidently, the thickness of the coatings has no significant influence on their impedance at lower frequencies.

**Conclusion.** The results of this work indicate that the impedance of both coatings was almost identical despite the obvious difference in their thickness, surface roughness, and microhardness. Only a slight deviation was observed at high frequencies due to their different thicknesses. Furthermore, all coated samples had an almost three times lower impedance compared to the pure untreated aluminium sample. This is most probably attributed to the much lower electrical contact resistance of those samples due to the coatings low reactivity with oxygen in natural free air conditions, as opposed to aluminium which rapidly forms isolating oxide layers atop its surface. Due to the thin nature of the coatings, their application in high-powered commutating electrical devices is unlikely, however, their application as intermediate protective layers in low powered stationary and commutating electrical contacts seems plausible. Due to the increased reactive capacitance of the coated samples, the influence of the skin effect on them increased greatly, making them unsuitable for implementation in high frequency circuits.

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