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Deposition and characterization of AlN thin films on ceramic electric insulators using pulsed DC magnetron sputtering

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A B S T R A C T

Porcelain electric insulators are fundamental support devices to act as holders for transmission lines. The exposition to pollutants environments such as industrial areas, deserts and sea air, containing carbon, sand and salt are examples that can reduce the devices dielectric property. The present investigation aims to develop and characterize hydrophobic aluminum nitride thin films, deposited on porcelain insulators surfaces, using a pulsed direct current magnetron sputtering (PDMS). An aluminum target with 99.999% purity was used as precursor and nitrogen 99.999% purity was employed. The film characterization was performed using AFM, FEG and FTIR. The surface resistivity was evaluated by four-point probe method. Different deposition times lead to different wettability characteristics, verified by the sessile drop method using a goniometer. The experimental results show the formation of a low roughness aluminum nitride film with hydrophobic properties over the glazed surface of a commercial porcelain electrical insulator.

1. Introduction

The outdoor environment where electrical insulators are exposed promote impurities accumulation, leading to degradation and a drastically reduction of its dielectric properties. In addition, if an impurity layer is accumulated, the flashover effect may cause a catastrophic failure in the device [1–3]. In order to reduce these problems, the electrical insulators are manually or automatically washed with water jets; a high-cost and often required procedure, that also exposes the system operator to a low safety situation [4]. Hafnium oxide (HfO), sulfur oxygen bonds (S–O) and titanium oxide films are pointed out in literature as suitable to increase dielectric and hydrophobic properties of electrical insulators [5–7].

Wettability is an important property of the material surface, as the ability of a surface to be wet or not, classified as hydrophilic or hydrophobic. The hydrophobic property promotes surface self-cleaning. The contact angle measurement (θ) between the solid/liquid interfaces is used to classify the surfaces. According to ASTM D7334-08, contact angles $<45°$ are hydrophilic, and $>45°$ are hydrophobic [8]. Other classifications are indicated by some authors as super-hydrophilic ($<10°$) or super-hydrophobic ($>150°$) [9,10]. Thereby, hydrophobicity is the surface ability to remain clean and dry, because the water slides down the surface, carrying away impurities [10].

Literature emphatically points out plasma techniques to grow such films. Several papers evaluate the nitrogen gas (N_2) flow rates, in relation to those of the deposited films characteristics [11–14].

Aluminum nitride (AlN) thin films present interesting characteristics to be applied in electric insulators such as: dielectric constant (band gap of 6 eV), piezoelectric behavior, mechanical resistance, and hydrophobic properties [12,15]. Although this application was not reported to date in the referred literature.

The present research aims to develop and characterize AlN thin films deposited on porcelain electrical insulators, to assure dielectric properties as well as self-cleaning hydrophobic surfaces, using pulsed DC magnetron sputtering (PDMS).

2. Experimental procedure

2.1. Substrate preparation

Porcelain electrical insulators are made of ceramic composition in the triaxial system, Feldspar–Kaolin–Quartz, covered by a thin glaze layer. The brown glaze in the electrical insulator surface is due to the presence of transition metal oxides Fe_2O_3, Cr_2O_3, CoO, ZnO and MnO. Samples were taken from the commercially available insulator

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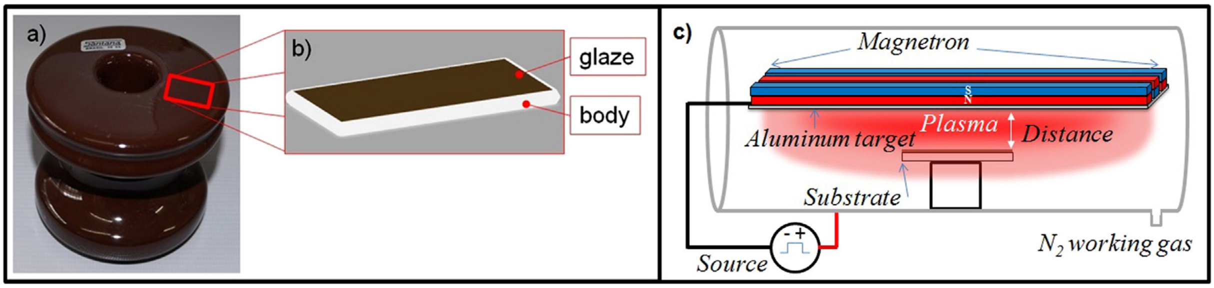

Fig. 1. (a) Commercial porcelain electrical insulator. (b) Details of substrates, showing the insulator body and glaze. (c) Schematic drawing of plasma equipment with indications of main parts.

(Fig. 1a) with dimension of 30 × 20 mm^2 each (Fig. 1b). They were cleaned with isopropyl alcohol in an ultra-sound equipment. Before the plasma deposition process, the substrates were maintained in a drying oven at 100 °C for one hour, already restored at room temperature by the time of deposition.

2.2. Plasma AlN deposition

Thin films of AlN coating were deposited employing a pulsed DC magnetron sputtering equipment. At Fig. 1c it is possible to visualize the plasma system that was used, in a schematic drawing.

The equipment possesses a planar conventional balanced magnetron with dimensions of 80 × 245 mm where the aluminum (99.999% purity) target is attached. A frequency source of 25 kHz with 15% duty cycle was employed.

The vacuum system is composed by a mechanical pump and a diffusion pump. While the mechanical pump depressurizes the vacuum chamber down to 0.3 Pa, the diffusion pump lowers the pressure to 3.5×10^{-3}. Working pressure of 0.3 Pa is again reached with the injection of N_2 (99.999% purity). The substrate immersion time to the plasma varied from 10 to 100 s, with 10 s increments. After deposition the atmospheric pressure is restored with N_2 addition. The sputtering was performed at room temperature, with a target substrate distance fixed at 50 mm. The plasma parameters of voltage, current, power and duty cycle were kept constant, and are indicated in Table 1. These plasma parameters were investigated elsewhere [16].

2.3. Film characterization details

The deposited films structural properties were investigated with field emission scanning electron microscope (SEM-FEG), Mira 3 from Tescam, and atomic force microscope (AFM), SHIMADZU SPM 9600, in contact mode. Advance contact angle measurements were performed with a goniometer in accordance with ASTM D7334-08 [1]. The chemical analysis of the films were made using Fourier Transform Infrared Spectroscope (FTIR), Perkin Elmer, in reflectance mode. Dielectric properties were determined at room temperature with the four-probe method using a Keithley 2410 source and a Keithley digital multimeter.

3. Results and discussion

Xu et al. [17] explained that for AlN films prepared using the magnetron sputtering method, the Al atoms sputtered from the target reacting with activated nitrogen atoms or ions, forming small Al clusters. The atoms condense on a surface finding preferential nucleation sites, such as lattice defects, atomic steps and impurities [18].

AFM measurements enable to characterize the film and substrate morphology, with micrographs corresponding to a 3D scanning area of 2 × 2 μm^2. Fig. 2a shows the original substrate, where surface scratches and an irregular surface roughness can be observed.

The morphological evolution of the films shown in Fig. 2b and c, are arranged accordingly to the deposition time with Fig. 2b showing the formation of isolated nanostructures, and the film coalescence start, along the substrate scratch defects. A higher surface area coverage can be observed in Fig. 2c, due to the microstructure evolution. By analyzing the film growth evolution through time, the process shows nucleation, island growth, impingement and coalescence of islands, grain coarsening, development of a continuous structure and film thickening. After 30 s a continuous film was formed in all samples (Fig. 2d).

Fig. 3 shows the cross-section microscopic analysis of a film deposited with 100 s with the average thickness of 545 nm (Fig. 3a).

Columnar film growth has been reported in literature due to substrate directionality [20,21]. In the present investigation, the deposition conditions led to refined microstructures. It can be observed the formation of micro cracks and surface defects. Similar results were reported by Mahmood for AlN deposition with DC reactive magnetron sputtering [19]. This deposition characteristic is related to the plasma system that was employed (PDMS) [22]. The combination of frequency (20 kHz), immersion time and duty cycle (15–50%) allows the deposition of a continuous film [24].

The flaw shown in Fig. 3b is possibly caused by the substrate defects although a higher deposition time is able to cover these with a continuous deposition [18].

Fig. 4 shows the measures of contact angle (θ) as a function of deposition time. The water drop spreads over the surface of the original substrate, as indicated in the photograph of Fig. 4, invalidating the θ measurement. For comparison effects, the original substrate contact angle was considered to be 10°.

It is clear from Fig. 4 that all treated samples show improvements in the contact angle value. The substrate treated with 10 s showed $\theta = 60°$. For increased deposition times, higher contact angle was observed, reaching $\theta = 85°$ for a 100 s deposition. The literature reports AlN films with $\theta = 72.9° \pm 5$ [15]. Higher contact angles increase the surface self-cleaning properties. The increased contact angle is related to the film morphology, where continuous films (Fig. 2c and d) exhibits enhanced morphology. As roughness measures can be deviated due to the substrate irregularities, a direct correlation between θ and roughness could not be established.

Table 1
Plasma treatment parameters for AlN films depositions.

Final pressure (Pa)	N_2 working pressure (Pa)	Voltage (V)	Current (A)	Power (kW)	Duty cycle (%)	Frequency (KHz)
3.5×10^{-3}	0.3	400	1.15	0.45	15	25

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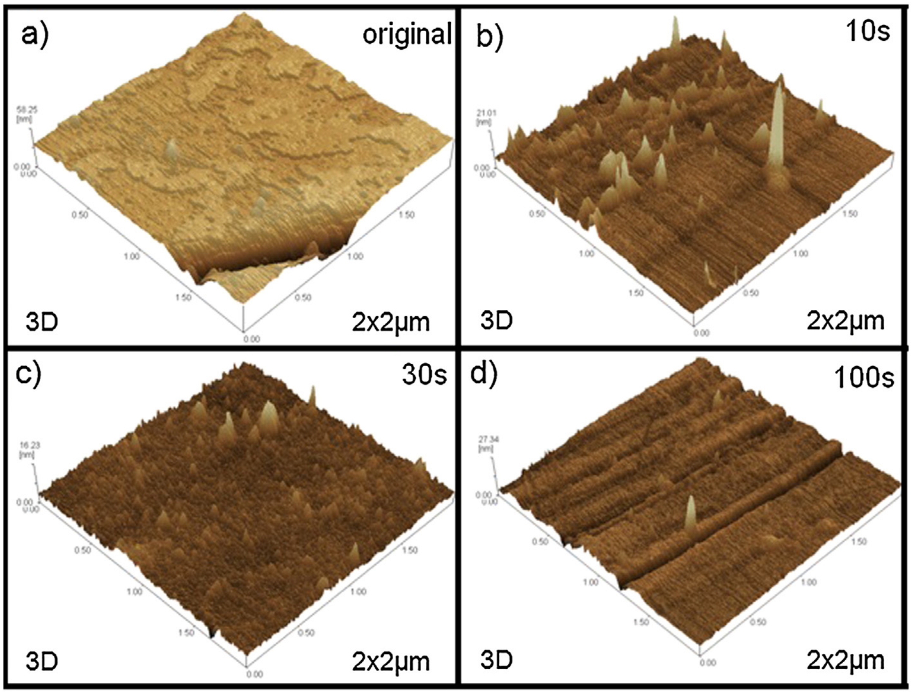

Fig. 2. AFM three-dimensional analysis, where (a) is the original substrate. The resulting surface morphology for different plasma AlN deposition times are shown: (b) 10 s, (c) 30 s, and (d) 100 s.

The formation of aluminum nitride was confirmed by FTIR spectrometry, characterized in the range of 400–4000 cm^{-1} and Fig. 5a shows these results for the deposited film with 100 s in comparison to the original substrate.

Fig. 5b demonstrates the spectrum amplification with indication to the 669 cm^{-1} peak that makes reference to the AlN. This band was observed only for the films deposited with times 100 s, because the thin coverage allowed interference with the substrate silicon content [11]. Several different positions have been reported for this peak in the literature, as lattice strain and impurities shift the peak, due to their effect on the vibrational energy of the average Al–N bond. At the work presented by Motamedi et al., the reference peak for the AlN is present in 672 cm^{-1} [23]. Furthermore, the FTIR peaks may be shifted from their characteristic position due to the residual stress in the AlN film caused by the sputtering process [25].

The asymmetric stretching modes of the Si–O–Si bond peaking at 1130 cm^{-1} and 1044 cm^{-1} is observed. The original substrate spectrum analysis makes reference to the glaze composition SiO_2–Al_2O_3–CaO–MgO–Na_2O–K_2O [26].

Electrical and optical properties of the electrical insulators are influenced by surface resistivity (ρ) [11,13]. The four points probe method indicates that the original substrate glaze surface have $\rho = 10^7\ \Omega\ cm^2$. The gases stoichiometry during the plasma deposition process has additional influence on the surface resistivity of AlN films and according to the literature [12,13,16] depositions with 100% nitrogen have $\rho = 10^6\ \Omega\ cm^2$. The elapsed deposition time evaluation indicates slightly

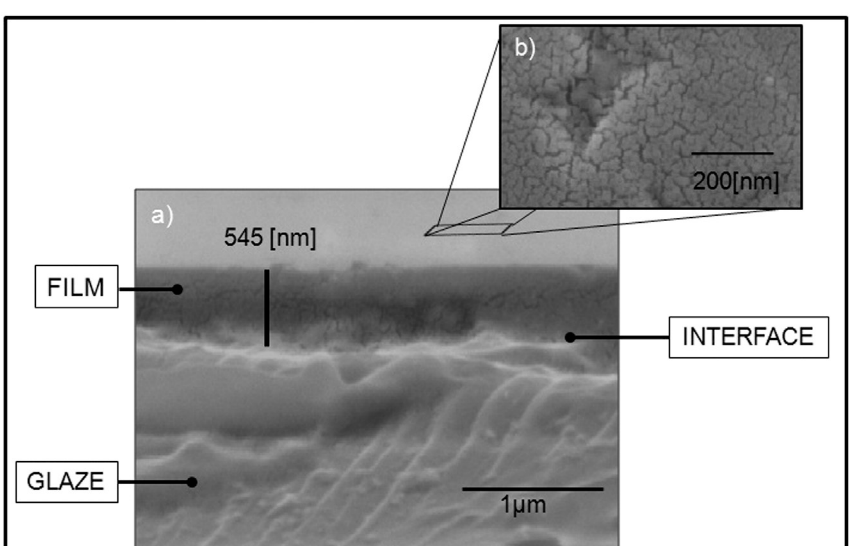

Fig. 3. (a) 100 s plasma deposited cross section showing the film thickness of 545 nm. (b) Film surface showing deposition imperfections and defects.

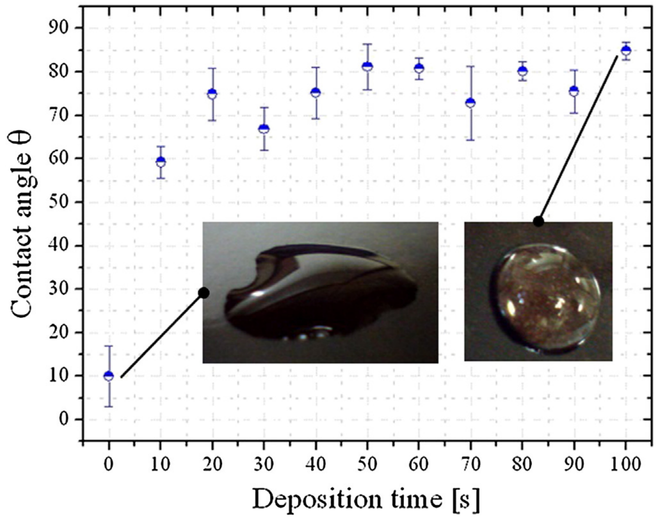

Fig. 4. Contact angle measured as a function of plasma AlN deposition time, showing hydrophobic behavior. A photograph of the original substrate is indicated, where a 10° contact angle was assumed.

improvement in the original substrate ($\rho_{10s} = 4.5 \times 10^7\ \Omega\,cm^2$; $\rho_{30s} = 6.2 \times 10^7\ \Omega\,cm^2$; $\rho_{100s} = 6.0 \times 10^7\ \Omega\,cm^2$). For electrical insulator application, it is mandatory that the hydrophobic films do not cripple the resistivity abilities of the material surface.

4. Conclusions

The morphological characterization of aluminum nitride films, deposited by PDMS plasma showed that both low roughness and thickness were obtained. The chemical composition of films investigated by FTIR confirmed the presence of AlN. Deposition times beyond 30 s with the indicated plasma parameters allowed the formation of hydrophobic films, with contact angles higher than 70°. The hydrophobicity properties achieved in this research are promising to develop self-cleaning ceramic electrical insulators, making electrical transmission lines more cost effective, safe and less maintenance demanding.

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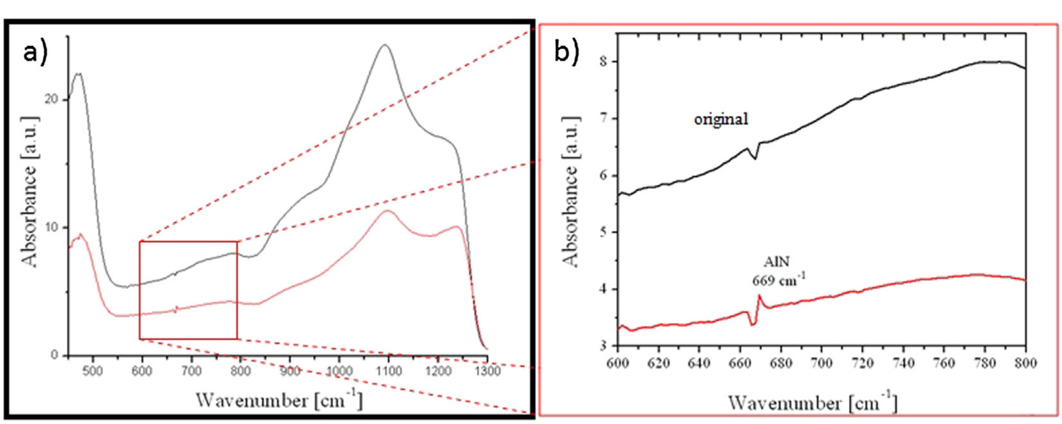

Fig. 5. (a) FTIR spectra for the original substrate and deposited AlN film. (b) Highlight of the 669 cm^{-1} peak.

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