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Comparison of thickness determination methods for physical-vapor-deposited aluminum coatings in packaging applications

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ABSTRACT

Methods used to determine the aluminum coating thickness on polymer films may not measure the geometrical thickness directly but may instead measure the mass or other properties, thus leading to different thickness values. Common methods include the determination of evaporation rates using a quartz crystal microbalance (QCM) and the quantitative analysis of dissolved aluminum ions by inductively-coupled plasma mass spectrometry (ICP-MS), which provide mass thickness values. Alternatively, atomic force microscopy (AFM) and interference (INT) across the step of a partially removed aluminum layer yield geometrical values, and optical density (OD) and electrical resistance (ER) measure other properties. We compared the ability of these methods to determine the thickness of aluminum coatings applied to polyethylene terephthalate (PET) and paper by physical vapor deposition. We measured ER using four-point probes, five-point probes, and eddy currents. ER and OD achieved high precision but low accuracy, showing that the resistivity and absorption coefficients of thin aluminum layers can deviate from bulk constants. When the constant values were adjusted, both methods achieved higher accuracy. ICP-MS and QCM values were similar, when a geometrical model was applied, and in comparison AFM and INT showed low precision but high accuracy. When the aluminum was applied to paper instead of PET, only ICP-MS generated reliable results. In summary, the values derived using these different methods are only in agreement when method-specific constants such as absorption coefficients and resistivity are suitably modified.

1. Introduction

The thickness and consistency of aluminum coatings have a strong impact on performance. In packaging applications, performance may be defined as the effectiveness as a gas barrier or the optical impression of decorative aluminum coatings. Gas permeation has been shown to decrease with increasing aluminum thickness up to approximately 60 nm [1] and only decreases further when the coating is 1–3 orders of magnitude thicker [2,3]. However, when measuring the relationship between permeability and aluminum thickness, the values reported and the techniques used to measure the thickness of the aluminum layer varied widely [2,4–10].

Coating thickness can be measured using methods that determine mass, geometry and other properties based on parameters such as electrical conductivity, light transmission, or the quantity of aluminum ions [11], but it is unclear whether the different instruments generate equivalent values (Fig. 1). For each type of instrument, some of the factors that influence the measurement are already known, and are summarized below. More detailed information can be found elsewhere [12].

Quartz crystal microbalances (QCMs) determine the “total mass thickness” of the deposited material based on the weight of the deposited aluminum, which includes both aluminum atoms and foreign atoms such as oxygen. This technique is accurate to within ~2%, but accuracy declines with increasing aluminum thickness [13–15]. Inductively-coupled plasma mass spectrometry (ICP-MS) similarly determines the “mass thickness” but in contrast to QCM only measures the pure aluminum. This is achieved by dissolving aluminum oxide and pure aluminum in sodium hydroxide before measuring the aluminum concentration [6]. The range of detectable concentrations is limited to approximately 0.001–0.1 µg/l for aluminum in aqueous solutions [16], and the results can be affected by interference between atoms with the same m/z ratio [17].

Atomic force microscopy (AFM) and interference (INT) determine

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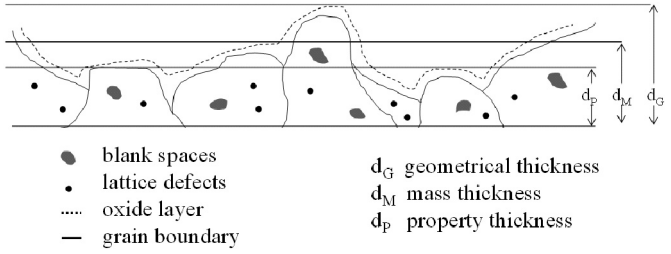

Fig. 1. Mass, geometrical and property thickness can vary widely because they are derived from diverse material characteristics such as light transmission, electrical resistance, or the quantity of metal ions.

the "geometrical thickness" of a sample. They capture the overall thickness of aluminum and aluminum oxide on a step produced by partial removal of the deposited aluminum layer. For INT measurements, both surfaces (substrate and aluminum) are covered with an additional 10-nm gold film to equalize the reflection characteristics. If the surface is rough, the reported thickness is higher than the average thickness of the layer [18]. Similarly, AFM does not separately record inclusions and voids, and the interaction between the AFM cantilever and the surface (topography and hardness) can affect the profile and the corresponding thickness values [19].

Finally, optical density (OD) and eddy current (EC) measure an indirect "property thickness". When using the OD method, a minimum transmission of ~0.03% (OD = 3.5) is useful [20]. Although greater thicknesses can be distinguished by using more sensitive equipment, the error increases due to heterogeneities and defects. The OD also decreases over time because the light-absorbing aluminum reacts with oxygen to form transparent aluminum oxide [4]. Furthermore, the OD is defined by the absorption coefficient α and the related extinction coefficient k (see Eq. (5)), and these values are highly dependent on the process conditions, grain size, coating thickness, and wavelength of the incident light [6,21,22]. When four-point (4P) and five-point (5P) probes are used to measure the electrical resistance (ER), a variety of factors can increase the resulting values. First, the instrument's electrical contacts may scratch the surface and cause cracks in the material. Second, oxide layers with a resistivity 20 orders of magnitude higher than the pure metal can act as an isolator between the aluminum and the contacts. Third, electrons can be scattered by the surface (particularly a rough surface) and by grain and island boundaries [23–30]. When the sheet resistance is measured by contactless EC methods, the values are influenced by the presence of aluminum oxide due to its extremely high resistivity. Furthermore, the sensitivity of EC measurements also depends on many other factors, such as the properties of the electromagnetic excitation field [31–33], the sensor-to-sensor distance, and the material thickness [34].

The aim of this study was to compare the thickness measurements produced by OD, electrical sheet resistance (4P, 5P and EC), QCM, ICP-MS, AFM and INT in order to determine whether the resulting values are similar, whether any differences can be explained and whether any of the methods are affected by the substrate beneath the aluminum layer, which in this study was either the polymer polyethylene terephthalate (PET) or paper. We use the data we obtained to draw conclusions about the structure of the aluminum layer.

These are important considerations because thickness and related parameters such as gas barrier efficiency, costs, and machine speeds are regularly compared using values derived using different methods. This can lead to misunderstandings and misinterpretations, and our findings will therefore be useful for researchers working on inorganic gas barrier coatings and industrial metallizers.

The data flow in this study is summarized in Fig. 2. The thickness determined by ICP-MS was used as a reference value for all the other methods. We then determined the material constants (absorption coefficient and resistivity) from OD, ER and ICP-MS reference values in order to characterize the structure of the aluminum layer.

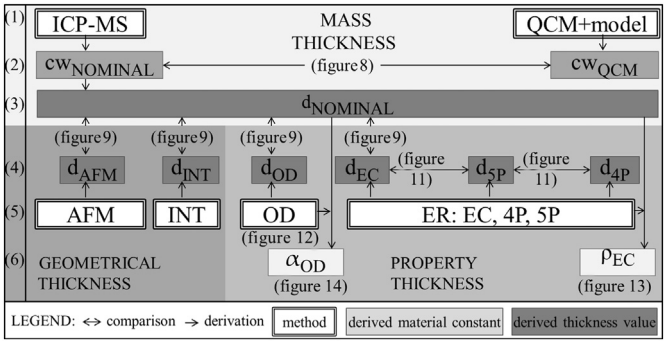

Fig. 2. Workflow for the experiments described in this article. Derivation of coating weight $cw_{NOMINAL}$ and cw_{QCM} from ICP-MS and QCM + model (1), comparison of both (2), derivation of a nominal thickness $d_{NOMINAL}$ from ICP-MS (3) and comparison of $d_{NOMINAL}$ with other methods (4,5), derivation of material constants (6) from $d_{NOMINAL}$ in combination with measured properties (5).

2. Materials and methods

2.1. Physical vapor deposition

The aluminum was applied by physical vapor deposition using an electron beam heater. The coating was applied in a 0.5 m × 1.0 m box coater (L560UV; Leybold Vacuum GmbH, Germany) at the Fraunhofer IVV (Fig. 3, right). This coater had been adapted for the roll-to-roll coating of polymer webs by adding winding equipment (deposition roll, unwinding, and rewinding; Lenze, Germany). The equipment was managed using L560 VAC Cluster Tool Controller (AIS Automation GmbH, Germany) software. The box coater was equipped with an E2M175 rotary vacuum pump (160 m^3/h) and an EH500 roots pump (505 m^3/h) both supplies by Edwards Ltd., UK, and a turbomolecular pump (850–1150 l/s, TMP 1000; Leybold Vacuum GmbH, Germany) to create a vacuum in the 10^{-4} Pa range. Remaining moisture in the chamber was extracted using a Meissner cold trap, and the deposition roll was water-cooled. The pressure was determined using a PPT-100 Pirani gauge and a HPT-100 hot cathode Bayard–Alpert–Pirani wide-range gauge, both from Pfeiffer GmbH, Germany. The EV M-10 electron beam source (270° configuration) was fitted with a Genius Carrera 10 kW high-voltage supply, all supplied by Ferrotec, Germany.

The aluminum was 99.98% pure and the coating thickness was varied by changing the web speed from 0.5 to 3.5 m/min in steps of 0.5 m/min at an evaporation rate of 4–4.5 nm/s. During the evaporation process, the pressure in the chamber was maintained at $5.6–7{\cdot}10^{-4}$ Pa. The moisture content of paper substrates is typically approximately 5% under ambient conditions, thus making it difficult to achieve a high vacuum. Therefore, the paper (Metalkote 65 g/m^2; Munksjö, Sweden) was dried at 50 °C for 4 days and then at 75 °C for 3 h in a Heratherm Oven (Thermo Fisher Scientific, USA) before the aluminum coating was applied. The polymer substrate was a 50-μm polyethylene terephthalate (PET) sheet (Melinex 401; DuPont Teijin Films, UK). The evaporation rate was monitored with a QCM (008–010-G10; Inficon, USA). The positioning of the balance in the vacuum chamber is described in Section 2.2.

2.2. Model for gas cloud expansion and aluminum thickness distribution

The crucible from which the aluminum vapor expanded was positioned immediately below the roll. The thickness distribution in cross direction (CD) was estimated on the basis of geometrical assumptions by considering two factors: (a) the expected gas cloud expansion and resulting thickness distribution in CD (Fig. 3, left); and (b) the web