Nanofilm Metal Layers As Vacuum Quality Sensors

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Abstract

A monitoring device for vacuum quality is realized by lowest cost single use oxygen sensors for vacuum insulation panels. They use the pressure dependence of oxide layer growth thickness on electrically measured metal nanofilms. These films were manufactured by e-beam evaporation, characterized in terms of resistance change with subsequent modeling of underlying mechanisms.

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1. Introduction

Energy saving devices continue to make inroads into the market. One sector in energy saving is heat insulations using nano physical effects like in vacuum insulation panels (VIP) that go into buildings and refrigerators. They consist of micro porous fumed silica enclosed in un-diffusible barrier film bags for vacuum tightness. As the latter are extremely sensitive to mechanical damage a monitoring device for vacuum quality is advised which in minimum works for the time span of production, storage, transport up to assembly in a final place. Besides fixed test systems the use of modified tire pressure sensors has been proposed and developed so far [1]. However, these sensors have not been able to cope with the cost limits up to now. Therefore low cost, single use vacuum quality sensor based on simplest nano film metal layers has been realized and characterized.

2. Idea, Theory and Design

As air is the medium which normally leaks into panels when damages in the barrier foil occur, the detection of the use of the chemical reactive oxygen in a VIP lies close at hand. The oxidation of bare, thin metal film is therefore one indicator for decreased vacuum quality. As Aluminium thin films are easy to prepare and show fast reactions in terms of oxidation kinetics and oxide layer growth with fast literature available, it served as best choice for checking the technical viability of using the following effect: The pressure dependence of oxide growth and
corresponding “final” thicknesses, where further increase in oxide thickness is almost stopped but still depending on surrounding pressure.

The oxidation of metals, according to Cabrera and Mott [2], is caused by the tunneling of electrons though the up-growing oxide driven by an internal electric field, resulting in the charge of adsorbed oxygen species at the oxygen-oxide interface and the charge of metal ions at the oxide-metal interface on the one and the diffusion of metal ions on the other hand. Cabrera and Mott did not directly include any pressure dependence in their theory, however some parameters still depend on the oxygen partial pressure like the tunnel probability or the sticking coefficient. Boggio [3,4] has extended this towards a pressure dependence in an explicit way. The resulting model of oxidation kinetics yields:

\[ X^{\frac{3}{2}} = \frac{\delta}{(V/X)^{\frac{1}{2}}} \cdot \ln\left( C \sqrt{P} \cdot t + C' \right) \]  

\( (I) \)

where \( X \) is the oxide thickness, \( \delta = 3h/(32m_e e)^{1/2} \) and \( V \) is the potential across the oxide \( X \). \( C \) can be described as the growth constant and \( C' \) is the constant of integration, which includes a possible previous oxide in this model. According to that theory detecting a leak in a barrier film of a VIP is possible by recording the resistance change of a thin metal layer. The oxygen pressure during the growth of the oxide should be available after evaluating the data.

In order to obtain a cost effective device the geometry of the sensor is a quite one large with a length of 28.5(±0.1) mm and a width of 1.2(±0.1) mm with nano layers onto a polymer PET film used as a substrate done by electron beam evaporation.

3. Technology and Measurement

3.1. Technology

For indicating possible substrate influences on the sensor performance different materials were tested resulting without noticeable differences. To maximize the overall sensor response (resistance increase caused by the influx oxygen) minimizing the remaining conductive path after the oxide growth is necessary, but is in conflict with the technology used for deposition. After cleaning copper contact pads were deposited onto the substrates at the ends of the 28.5 mm structure in order reduce contact resistance. On these pads aluminum layers were deposited at a base pressure of 5·10⁻⁶ mbar with rate of approx. 8 Å/s to a total thickness of about 7 nm. The thickness and rate were recorded by a quartz microbalance rate monitor (QMB).

3.2. Measurements

Subsequent to the deposition of the sensing metal layer the oxidation was started by admitting air into the vacuum chamber. The resistances of two sensors were electrically recorded. After reaching the saturation value of the resistance the pressure inside the deposition chamber was raised again in order to obtain atmospheric pressure by several steps. A typical resistance-time plot is shown in figure 1, where four pressure steps are visible. The resistance difference between both identical devices is assigned to different positions of the sensors during the deposition resulting in different nominal layer thicknesses. The thickness of the devices in fig.1 is 6.8 nm (reading value of the QMB) and the initial raise in pressure to 1.5 mbar (approx. inner pressure of a VIP) shows no further resistance change after reaching the saturation. Therefore the storing of the sensor in the panel should be possible for
an unlimited period of time. Increasing the pressure from 1.5 mbar to 10 mbar results in a resistance change of 10 Ω, which is acceptable for electronic readout and surveillance of vacuum quality.

![Graph showing resistance change over time for two sensors exposed to various pressures.](image)

Fig. 1: Resistance change over time for two sensors exposed to various pressures

4. Data Modeling

Resistances as recorded and corresponding oxide layer thicknesses are compared. As the resistivity of nanometer thin layers is vastly deviating from common bulk values due to the scattering of electrons at the surface [5,6], grain boundaries [7,8] or the quantum size effect [9,10] the evaluation of the sensor performance in terms of resistivity gets quite complicated. One approach to estimate such nonlinear behavior is to investigate the resistivity obtained in our preparation separately and then use of this parameter for transforming resistances into oxide layer thicknesses. Another important parameter for the application as a single use sensor is the lifetime in the vacuum panel and experiments as well as figure 1 show acceptable values for it.

Using a thickness depending resistivity ρ* , a transformation of R(t) into oxide thicknesses d(t) is possible. The data of d(t) are comparable to other studies of aluminium oxidation [11]. In approximation, where l, w and ρ* are the length, width and the resistivity of the conductive layer and the initial resistance R_0. Y reflects the ratio of in- and on-growing oxide layer thickness.

\[
d(t) = \rho^*(d) \cdot \frac{l}{w} \left( \frac{1}{R(t)} - \frac{1}{R_0} \right) y \tag{2}\]

The comparison with respect to the transformation is shown in figure 2 where error bars reflecting the Gaussian uncertainty for vanishing metal paths have been added. The calculated graph was computed by using equation 1, with V/X=0.017·10^{-10} V/m, δ=1.46·10^{-10} V^{1/2}, m=1.2·10^{-19} m^3, C_0 = 91.22 min^{1/2}torr^{1/2} as the parameters, which is almost over the whole oxidation time in a good agreement with the measured data beyond the first 100 seconds. Even for the final step towards atmospheric pressure the model remains valid in principal. The initial difference can be referred to the change in the Volta potential V for the early stage of oxidation and the sub-nanometer range of oxide thickness.
5. Discussion

Using the theory of pressure dependence for the oxidation of metals a vacuum quality or oxygen sensor may be realized by nano film metal layers in quite simple geometries. They are suitable for monitoring the vacuum quality inside a vacuum insulation panel. The calculation and the measurements of the oxide thicknesses for aluminum nanofilms comply sufficiently and whilst the resistance change themselves for the pressure steps from 1.5 mbar to 10 mbar - which describe the application in a VIP quite well — are found in a range which is easily accessed by un-extensive electronic readout circuitry.

References

[1] Fraunhofer IMS, Duisburg, Germany, Press Release March 2010