Scripta Materialia xxx (2015) xxx–xxx

Contents lists available at ScienceDirect

Scripta Materialia

journal homepage: www.elsevier.com/locate/scriptamat

Evaluation of Atomic Layer Deposition coating as gas barrier against hydrogen gas and humidity

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ARTICLE INFO

Article history:
Received 29 April 2015
Accepted 10 May 2015
Available online xxxx

Keywords:
Atomic Layer Deposition
Gas barrier
Hydrogen degradation
Varistor
Diffusion

ABSTRACT

Effectiveness of HfO_2 Atomic Layer Deposition coatings has been studied on ZnO varistors by *I–V* tests, impedance spectroscopy, and highly accelerated life test. Based on impedance spectroscopy analyses, the proton diffusion coefficient was measured to be 400 K times less in the coating. Transmission electron microscopy analysis shows that Atomic Layer Deposition films are continuous and conformal. After exposure to high temperature, partial crystallization was detected in the coating and increases proton diffusion coefficient by 150 times.

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UNCORRECTED PROOF

Varistors or variable resistors are passive components, which are used in protection against voltage surges, that shunt the excess charge to the ground [1–4]. The design is typically around ceramic materials based on ZnO with dopants and sintering aids added to control the nature of the controlled breakdown process and minimize the leakage in the stand-by operational condition [4,5]. The grain size and the grain boundary compositions are critical and are back-to-back Schottky barriers controlling these conditions [6,7,1,3]. There is concern about the packaging of varistor components at the atmosphere in which they are exposed to humidity or hydrogen gas [8]. The source of hydrogen gas could, for example, be the out-gassing of corrosive atmospheres from incompletely cured epoxies and or electrolytic capacitor seal failure [9–11].

There have been earlier studies on the atmosphere sensitivity to varistors, such as the work of Sonder et al. [12] who have studied systematically the effects of reducing atmosphere on the resistivity degradation of ZnO varistors. In their case, a reductive agent of CO and different percentage of oxygen and inert gas at the interval temperature of 150–800 °C were considered. It was found that ZnO varistors can be degraded by annealing at 260 °C in a CO/CO_2 atmosphere, and showing resistance can decrease from 10^{10} to 10^4 Ω after 33 h of exposure to CO/CO_2. In addition, there are additional reports of resistivity degradation of ZnO varistors due to hydrogen gas exposure [11,13]. It will be shown in this report that the leakage current can increase from 10^{-8} to 10^{-4} A at 170 °C after one hour exposure to hydrogen gas.

ALD (Atomic Layer Deposition) coatings demonstrate a good gas barrier property [14–17] on various substrates, which makes them promising to hinder the degradation process. In this letter, the effect of exposure of ZnO varistors to forming gas (4% hydrogen and 96% nitrogen) and humidity has been studied, and the application of ALD coating as a gas barrier layer has been evaluated. In addition, the proton diffusion coefficient has been measured for both ZnO varistor and HfO_2 ALD layers to demonstrate effectiveness as gas and humidity barriers for ZnO based varistors.

A commercial ZnO varistor was cut to 15 × 15 × 1.4 mm and ground up to 1200 grit sandpaper, then a circular Pt electrode with area of 5 mm^2 was sputtered to the center of both sides of samples. Impedance spectroscopy was applied, by SR-830-DSP Lock-in connected to a charge measurement system (the test was conducted in Material Characterization Lab of the Pennsylvania State University), to trace the degradation in grain and grain boundaries at 135, 155, and 175 °C, when they were exposed to forming gas (4% hydrogen and 96% nitrogen) for 3 h.

HfO_2 ALD coating was applied around the devices using 150LE, The Kurt J. Lesker Co. and the precursor of TDMAH, tetrakis (dimethylamino) hafnium (IV) ($C_8H_{24}N_4Hf$), and water. Dose times of the precursor and water were 0.15 and 0.03 s, followed by the purge time of 10 s at the temperature of 200 °C and the pressure of 400 mtorr. The growth rate was measured 1.3 Å/cycle.

Another set of tests was leakage current measurement to monitor the amount of resistivity degradation. The varistors with different coating thicknesses were exposed to forming gas in the

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http://dx.doi.org/10.1016/j.scriptamat.2015.05.013
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interval temperature of 80–290 °C; for every 20 °C increment, they were held for 30 min, while the leakage current was measured every second under an applied voltage of 5 V. A Highly Accelerated Life Test (HALT) was executed by Temperature Humidity Chamber (Blue M, Illinois, USA) at the temperature of 90 °C and humidity of 85% for 120 h, under 100 V applied voltage on the coated and uncoated samples. TEM samples were obtained by FEI Helios NanoLab 660 FIB/FESEM. The TEM analysis was executed by JEOL 2010F.

Impedance spectroscopy analysis is an effective method to monitor the relative changes in resistivity and capacitance in grain and grain boundary microstructures. We represent the impedance data (Z′, Z″) in the complex plane in the form of Nyquist or Cole–Cole plots, noting the changes with the experimental variable of different exposure times in Figure 1(a). It was found that Cole–Cole plots can be fitted well with the two impedance element equivalent circuits shown in Figure 1(b), the electrode contribution is negligible in the ZnO varistor, and the largest contribution comes from grain boundary barriers. Our approach is consistent and builds on the analysis of Andres–Verges and West [18], where the grain impedance can be approximated with a pair of ideal capacitor and resistor. The capacitor is representative of the transient charge storage in grains and the resistor the bulk resistivity of ZnO crystals. For the grain boundary circuit representation, another element, CPE (constant phase element [19]), is added to consider the inhomogeneity over all the grain boundaries [20].

The resistance of grains and grain boundaries under different hydrogen gas exposure times is shown in Figure 1(c). The resistance of the grain boundaries at the beginning of the exposure is 100 times higher than the resistance of grains at the end of exposure. While the GB resistance decreases an order of magnitude, the grain resistance is essentially invariant under the gas exposure conditions used here. The change in GB resistance can be related to proton concentration acting as a donor dopant reducing the interfacial grain boundary resistance [11].

The change in GB resistance can be used to determine the diffusion of hydrogen into the grain boundaries, by defining appropriate boundary conditions and solving Fick's law, one can estimate diffusion coefficient of protons at 135 °C in grain boundaries [21]. One of the boundary conditions can be concluded from the fact that the entering rate of total hydrogen ions ($\frac{dN(t)}{dt}$) to the device is proportional to the concentration difference between the atmosphere (C_0) and the surface (C_s), which can be represented as:

$$\frac{dN(t)}{dt} = \alpha(C_0 - C_S) \quad (1)$$

where α is a proportionality constant.

The other boundary conditions are obtained based on the assumption that the diffusion system is semi-infinite. Here, we need to consider an additional assumption, which is that the Pt electrode is not a barrier against proton diffusion. Regarding the hydrogen diffusion coefficient in Pt [22,23] and ZnO [11,24–26], the diffusion coefficient in Pt is several orders of magnitude higher than the diffusion coefficient in ZnO in the temperature interval of the present work. So the above mentioned assumption is valid.

The same impedance spectroscopy tests were executed at 155 and 175 °C, and the calculated diffusion coefficients are shown in Figure 1(d). One can find the best line that passes those three points, and find the activation enthalpy for proton diffusion, as 0.88 eV, which is fairly close to the reported values of 1.21 [25] and 0.91 eV [11] for proton diffusion in ZnO. However, it is reported as 0.17 eV [24] elsewhere. Nickel [26] has thoroughly studied the proton diffusion coefficient in single and polycrystal ZnO thin films. He argued that the activation enthalpy can depend on temperature and reported 0.75 eV for ZnO poly crystals at 155 °C. It should be noted that the resultant diffusion coefficients

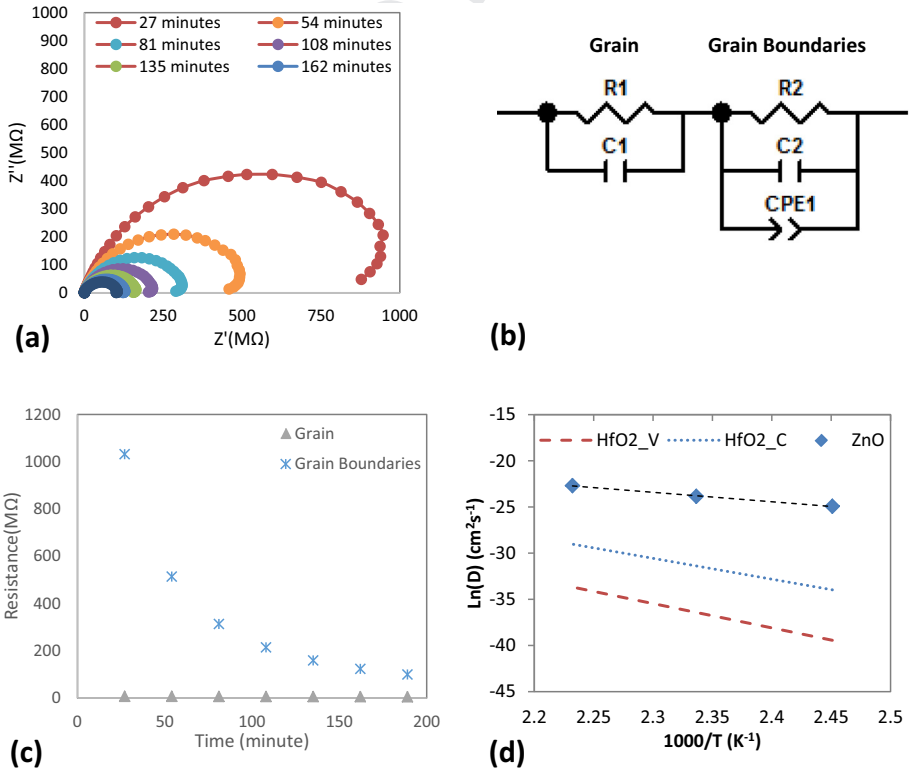

Figure 1. (a) Cole–Cole plots of the ZnO varistor exposed to forming gas at 135 °C at different exposure times; (b) equivalent circuit; (c) resistance of grains and grain boundaries vs. gas exposure time at 135 °C; (d) proton diffusion coefficients vs. reciprocal temperature in grain boundaries of ZnO varistors, virgin HfO_2 ALD layers and crystalized HfO_2 ALD layers.

Please cite this article in press as: D. Sohrabi Baba Heidary, C.A. Randall, Scripta Mater. (2015), http://dx.doi.org/10.1016/j.scriptamat.2015.05.013

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