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Investigation of humidity sensors based on Sn-O-Te films by impedance spectroscopy

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Thin Sn-O-Te films with a thickness of 60 nm have been deposited by co-evaporation of Sn and TeO_2 on alumina substrates with interdigitated silver-palladium electrodes. During the co-evaporation a chemical reaction between the two substances takes place, resulting in the formation of a Sn-oxide matrix and finely dispersed phases of Te, Sn, TeO_2 or SnTe, depending on the atomic ratio of Sn to Te ($R_{Sn/Te}$). To study the morphology and structure as well as to determine the atomic ratio $R_{Sn/Te}$ of the films, electron microscopy techniques (TEM, SAED) and analytical methods (EDS in SEM) have been applied. The electrical properties of the sensors studied have been investigated in the frequency range of 20 Hz – 5 MHz using a Precision Impedance Analyzer. The measurements have been taken on samples placed in a controlled humidity and temperature chamber. The characteristics of the resistance *R*, capacitance *C*, impedance *z* and phase θ as functions of relative humidity *RH*%, the frequency dependences of *R*, *C, z* and θ, the Nyquist plots and equivalent electrical circuits of the sensors have been obtained. As a result, the relation between the type of water adsorption, impedance spectra and the properties of the films as humidity sensors are presented in this paper.

Keywords: humidity sensors, impedance spectra, tin dioxide

INTRODUCTION

Humidity measurement and control are an important task in industry, agriculture, medicine, for storage and transportation of various products and raw materials, pieces of art, etc. Various types of humidity sensors are employed in all these fields [1].

Thin vacuum deposited films, obtained by co-evaporation of Sn and TeO_2, are an object of intensive study in the Institute of Optical Materials and Technologies [2] since they are a base for development of gas sensors, conductive films etc. This paper presents a detailed investigation on the electrical properties, impedance spectra and equivalent electrical circuits of as-deposited Sn-O-Te films, intended for humidity sensors.

EXPERIMENTAL

Sample preparation

The films were obtained by thermal co-deposition of Sn and TeO_2 from independently heated Knudsen type cells, under vacuum better than 10^{-4} Pa [3]. Alumina plates of 18x10x0.5 mm with interdigitated silver-palladium electrodes, held at ambient temperature, were used as substrates. The condensation rates of both substances were controlled separately during the whole evaporation process using quartz crystal monitors. Samples with two different values of $R_{Sn/Te} < 1$ were prepared, which have been previously shown [4] to be sensitive to ambient humidity. The samples with $R_{Sn/Te} \approx 0.86$ were marked as S1, and with $R_{Sn/Te} \approx 0.6$ - as S2.

Measurements

Structure and composition - The amount of both substances ($R_{Sn/Te}$) and the thickness of the films were calculated on the base of the measured evaporation rates using computer programs as described in [5]. The data obtained for $R_{Sn/Te}$ were controlled by Energy Dispersive Spectrometry (EDS) in SEM (Philips 525/EDAX 9900), and for the film thickness – by a profilometer Talystep (Rank Taylor Hobson). Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) (HRTEM JEOL JEM 2100) were used for studying the morphology and

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structural characterization of the films. The samples intended for TEM were evaporated on glass plates with a water soluble PVA sub-layer. Their thickness (60 nm) was suitable for the direct imaging in TEM.

Electrical characteristics and parameters - The measurement of the impedance characteristics of the samples was taken by Precision Impedance Analyzer 6505P product of Wayne Kerr Electronics Ltd, in the frequency range of 20 Hz to 5 MHz and 500 mVrms of the excitation signal. The samples were placed into a chamber of the Humidity Generator VAPORTRON H-100BL, manufactured by BUCK RESEARCH INSTRUMENTS L.L.C., which provides conditioning of accurately controlled humidity ranging from 15 to 95% with maximal deviation of up to ±1.5% of relative humidity.

RESULTS AND DISCUSSIONS

Structure and composition

As seen in Fig. 1, the films with $R_{Sn/Te} \approx 0.8$ have a fine-grained structure and the selected area electron diffraction does not indicate the presence of a crystalline phase. This is in accordance with previous results of ours which have shown that the as-deposited films with $R_{Sn/Te}$ varying over a wide range (0.3÷2.3) are amorphous and exhibit a nanosized grain and columnar structure [3, 4].

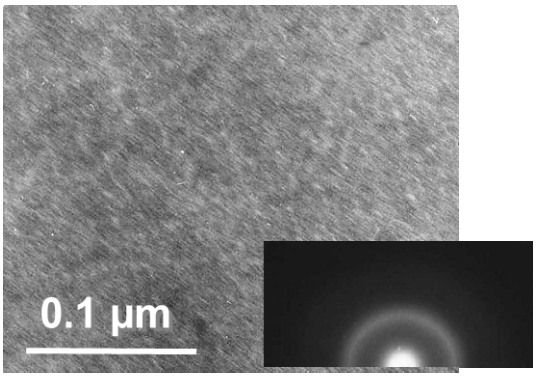

Fig. 1. TEM image and SAED pattern of 60 nm thick layer with $R_{Sn/Te} \approx 0.8$.

The sensing properties of the films are strongly dependent on their composition. That is why it was important to check the reliability of the computer calculations described above and the preparation reproducibility. The calculated $R_{Sn/Te}$ values were compared to the respective data obtained by EDS-analyses in SEM and a very good coincidence was found (deviation ~ 2%) [2].

Electrical measurements

Measurements have been taken with alternating current to avoid the effect of sample polarization. Figure 2 and Fig. 3 present the characteristics $R = f(RH)$, $C = f(RH)$, $z = f(RH)$, $\theta = f(RH)$ of samples S1 and S2, respectively, at a temperature of 25°C, where R, C, z and θ are their electric resistance, capacitance, impedance and phase, and RH is the relative humidity.

For all parameters investigated, the ranges of their changes are largest at 20 Hz and decrease with a rise in frequency. These changes are insignificant above 10 kHz. From a comparison of the characteristics $R = f(RH)$, $C = f(RH)$, $z = f(RH)$ at 20 Hz, it can be concluded that electrical resistance R has the greatest relative change R_{max}/R_{min} in the range from 15 to 95%RH for both samples compared to the relative changes C_{max}/C_{min} and z_{max}/z_{min}. A large change in phase θ is observed from around 86° down to around 10° at a frequency of 20 Hz, but within the narrower range of 65 to 93% RH. Therefore the parameter R is the most informative and for that reason it is used to compare the sensitivity S_R of the different elements. The sensitivity S_R has been determined for different segments of the sensor characteristics and is given by the slope of the characteristic, i.e. $S_R = |\Delta R/\Delta RH|$, where ΔRH is the relative humidity change and ΔR - the respective resistance change for a specific segment. The sensitivity to humidity is the lowest at low values of humidity for both samples. It is observed for sample S1 that sensitivity is greatly enhanced at humidity values of over 45%RH and at a frequency of 20 Hz the maximum value of S_R within the range of 45-73%RH reaches 106.7 MΩ/%RH, and after that it gradually decreases. For sample S2 at a frequency of 20 Hz the maximum sensitivity is observed within the range of 65-73%RH and it reaches 46.6 MΩ/%RH, and after that it gradually decreases. Consequently the maximum sensitivity of sample S1 is about twice as high as the sensitivity of sample S2. Besides, the humidity range with high sensitivity is wider for sample S1. The range of resistance change at a frequency of 20 Hz for sample S1 is of about 3 orders, and for sample S2 it is of about 2 orders. The resistance of sample S1 at 93%RH decreases up to about 1.7 MΩ, and for sample S2 – up to 6.5 MΩ.

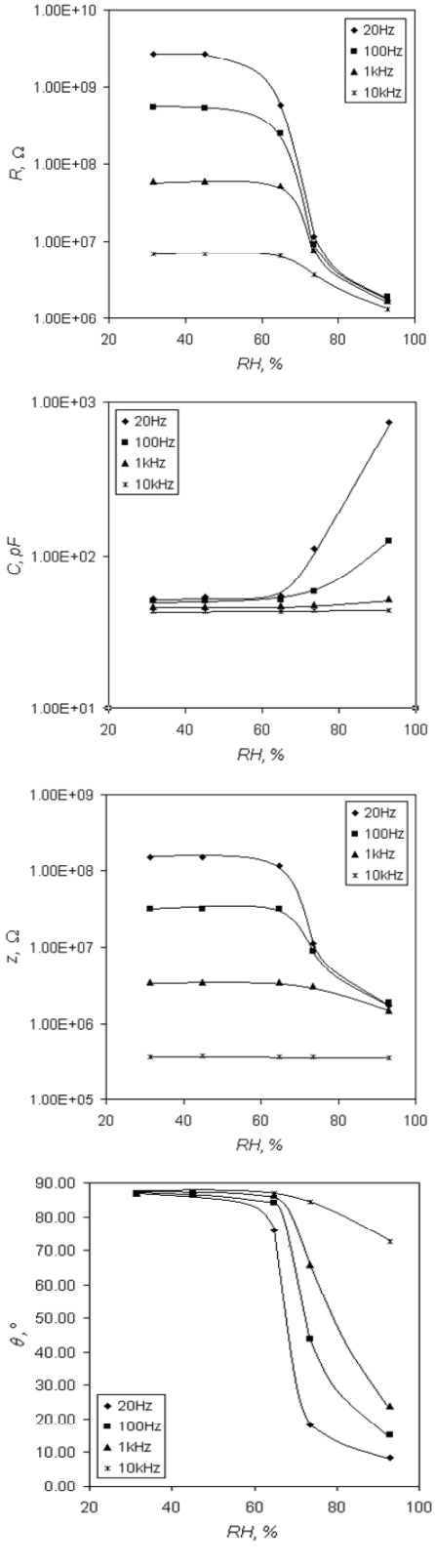

Fig. 2. Characteristics: $R = f(RH), C = f(RH),$ $z = f(RH)$ and (d) $\theta = f(RH)$ of samples S1 at a temperature of 25°C and for various frequencies.

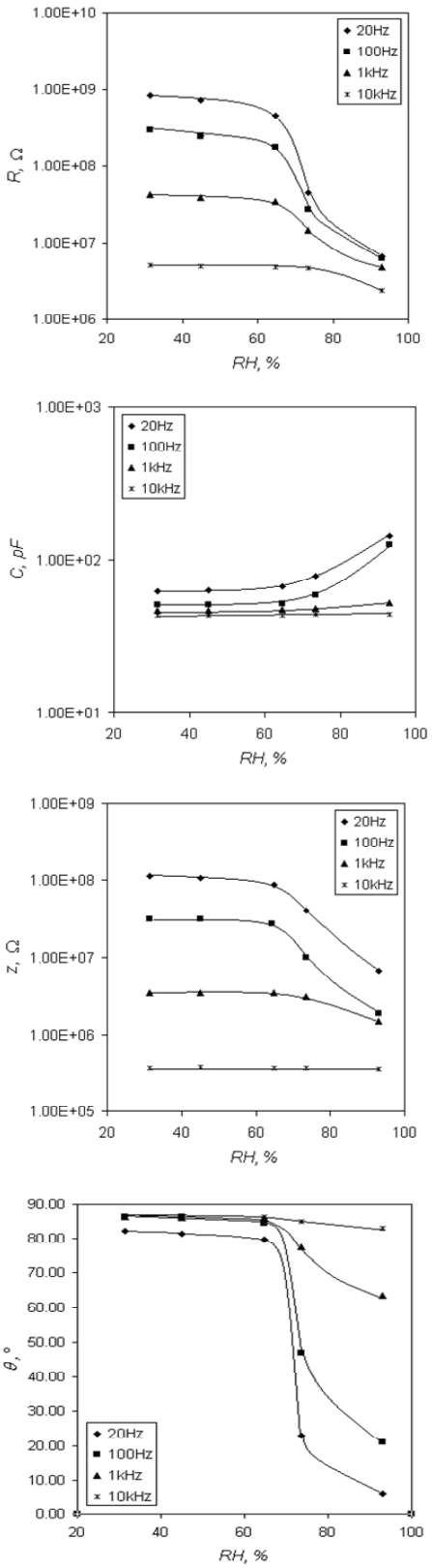

Fig. 3. Characteristics $R = f(RH),$ $C = f(RH),$ $z = f(RH)$ and $\theta = f(RH)$ of samples S2 at a temperature of 25°C and for various frequencies.

The results obtained show that better properties as humidity sensors are observed for the layers with the higher $R_{Sn/Te}$ value. They are in a very good agreement with earlier published data about the influence of $R_{Sn/Te}$ on the humidity sensing behaviour and the very high sensitivity measured at a frequency of 0.2 Hz [2].

Since with rising frequency the resistance of the layers decreases at low values of humidity, which is favourable for practical applications, it is possible to use them in measuring circuits at higher frequencies as well (up to 1 kHz). Then their maximum sensitivity decreases but it is sufficiently high (5.1 MΩ/%RH for layers S1 and 2.2 MΩ/%RH for layers S2) for such applications.

Impedance spectra

Humidity sensing elements of metal oxide materials are characterized by water adsorption and condensation [6]. The resistance of the investigated sensor elements of metal oxide type decreases with an increase in the relative humidity due to the chemical adsorption and physical adsorption and condensation of water molecules. In the initial stage of adsorption, a chemical adsorption of water molecules on the surface of the respective sensors takes place [7, 8]. The active role in this process is played by metallic atoms, M. They interact with the water molecules to form hydroxyl groups M-OH. In this way the surface of crystals is covered by a monolayer of water molecules. After the formation of the first chemically adsorbed film a physical adsorption of water molecules on it occurs [9, 10]. The mechanism of water adsorption described is closely related to its effect on the impedance characteristics of the samples and on the impedance spectra, respectively. To clarify this relation based on the frequency characteristics $z(f)$ and $\theta(f)$, the Nyquist plots of reactive resistances on active resistances for samples S1 and S2 at various *RH* and a temperature of 25°C have been obtained. Within the frequency range of 20 Hz to 5 MHz the impedance spectra and equivalent electrical circuits for the sensor elements are shown in Fig. 4.

At low humidity values (up to about 45% RH for the investigated samples), these plots are close to a straight line which corresponds to Nyquist plots of the base sensing material [9]. When humidity rises above these values (in this case above 45%RH) the Nyquist plots are arcs from semicircles of very large radii, and their equivalent circuit consists of resistance R_1 and capacitance C_1 connected in parallel, shown by circuit (I) in Fig. 4.

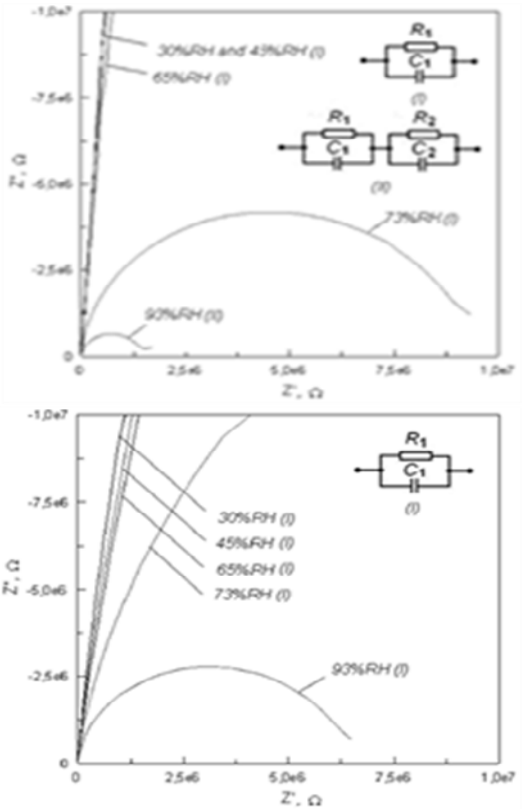

Fig. 4. Nyquist plots and equivalent electrical circuits for: (a) sample S1 and (b) sample S2 at a temperature of 25°C and at various *RH*.

This type of impedance spectra can be explained by the prevailing type of electron conduction through the base sensing material and the adsorbed water on the sensor surface in the stage of chemical adsorption [9, 10]. With increasing RH (above 65%RH) the chemisorption enhancement and leakage current increment lead to growing the curvature of the arc and it gradually approximates a complete semicircle (73%RH for sample S1 and 93% for sample S2). Simultaneously, a decrement in the sample impedance is observed which is related to the enhancement of this conduction. When humidity increases further, ionic conduction also appears as a consequence of the presence of physical adsorption as well. It is exhibited by the initiation of a second semicircle with a very large radius in the Nyquist plots within the range of lower frequencies [10]. This additional part of arc is observed in the Nyquist plots of sample S1 at 93%RH. In this case in the equivalent electrical circuit a second group of R_2C_2 is added which is explained by the appearance of conduction of ionic type. It is represented by circuit (II) in Fig. 4. Therefore, the entire conduction mechanism is a combined action of both electron and ionic

conduction [9, 10]. The electron conduction enhancement and the ionic conduction appearance lead to a serious reduction in the impedance of samples when humidity rises. For sample S1 this reduction is more significant. The obtained relation confirms the better humidity sensing properties of sample S1, compared to sample S2.

CONCLUSION

Thin Sn-O-Te films obtained by vacuum co-deposition of Sn and TeO_2 could be successfully used as humidity sensors operating at room temperature. Films with $R_{Sn/Te} \approx 0.86$ possess better humidity sensing properties than films with $R_{Sn/Te} \approx 0.65$. The appearance of electron and ionic conduction is related to chemical and physical adsorption of water on the sensor surface.

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ИЗСЛЕДВАНЕ НА СЕНЗОРИ ЗА ВЛАЖНОСТ НА БАЗАТА НА Sn-O-Te СЛОЕВЕ ЧРЕЗ ИМПЕДАНСНА СПЕКРОСКОПИЯ

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(Резюме)

Получени са тънки Sn-O-Te слоеве с дебелина 60 nm чрез термично вакуумно отлагане на Sn и TeO_2 върху керамични подложки от Al_2O_3 със сребърно-паладиеви гребеновидни електроди. По време на съвместното изпарение протича химическа реакция между двете вещества, която води до образуването на матрица от Sn оксиди и финодиспергирана фаза от Te, Sn, TeO_2 или SnTe, в зависимост от атомното съотношение между Sn и Te ($R_{Sn/Te}$). За изследване на морфологията и структурата, както и за определяне на атомното съотношение $R_{Sn/Te}$ в слоевете са използвани методи на електронна микроскопия (TEM, SAED) и аналитични методи (EDS в SEM). Електрическите свойства на изследваните сензори са проследени в честотния диапазон 20 Hz – 5 MHz с помощта на прецизен импедансен анализатор. Измерванията са проведени върху образци, поставени в камера с контролирана влажност и температура. Получени са характеристиките на активното съпротивление R, капацитета C, импеданса z и фазата θ като функция на относителната влажност, честотните зависимости на R, C, z and θ, комплексните импеданси (Nyquist plots) и еквивалентните електрически схеми на сензорите. Като резултат е показана връзката между типа на адсорбцията, импедансните спектри и свойствата на изследваните образци като сензори за влажност.