CHEMISTRY LETTERS, pp. 1729-1732, 1990.

Preparation of Niobium Oxide Films as Humidity Sensor

Hideyasu TSUIKI, Takeaki SHIMANOUCHI, Naoyuki TAKAHASHI,
Noriyoshi KAKUTA, and Akifumi UENO*
Department of Materials Science, Toyohashi University of
Technology, Tempaku, Toyohashi, Aichi 440

Niobium oxide films were prepared on a glass plate by dipping in a viscous solution of niobium penta-isopropoxide dissolved in 2-propanol. The films had humidity-sensitive electrical resistance with good selectivity and an extremely high surface area even after the iterative adsorption/desorption cycles of water vapor, suggesting that the films could be used as a humidity sensor element.

A sintered ferrite such as $MgFe_2O_4$ has been practically used as a humidity sensor,[1) but the following problems have been still pointed out to be overcome; one is a poor durability of the ferrite sensor for adsorption/desorption cycles of water vapor. Some of the water vapor adsorbed hardly desorb from the ferrite surface and accumulate, resulting in less accuracy of the humidity measurements. This problem has been tentatively overcome by so called "cleaning" method, making the water vapor release from the surface by heating it at 400 °C. Several times of "cleaning", however, result in the change in the surface structures of the sensor element, suggesting again a reduced accuracy of measurements. Recently, a sensor consisting of $ZnCr_2O_4/LiZnVO_4$ has been reported to have an improved durability for the iterative adsorption/desorption cycles,[2) no "cleaning" being required for 22 months. Another problem is the low selectivity for water vapor adsorption on the ferrite surface, since alcohols and carbon dioxide adsorb on the ferrite surface as well, which also affects upon an accuracy of the humidity measurements.

Thus, the purpose of this work is to develop a new element to be employed in a humidity sensor. The element must satisfy the conditions mentioned above. Instead of sintered ceramics, we employed niobia films as a sensor element, partially because of a fundamental interest in modified electronic properties of thin films[3) and partially because of the fact that niobia works as an acid catalyst even in an aqueous solution.[4)

Niobia films were prepared by dipping a glass plate(26x38x1mm) into a solution of niobium penta-isopropoxide dissolved in 2-propanol, the solution being rather viscous when stirred at 25 °C for 30 min. The glass plate was then withdrawn from the solution with a pulling rate of 150 mm/min, followed by drying and calcining at 400 °C for 4 h. A broad peak was observed at $2\theta=30.5$ in the X-ray diffraction spectra(Cu Kα irradiation using a Ni filter) of calcined niobia films, indicating the formation of finely-divided NbO_2 crystallites in the niobia films. The film surface was so smooth as to be within ± 50 Å of roughness, measured by a surface roughness tester equipped with a diamond probe.

Thickness of the calcined films is well controlled by the concentration of niobium penta-propoxide dissolved in 2-propanol,(see Fig. 1) and the films of 0.3 μm thick were subjected to various measurements as a standard sample. The specific surface area of the films was measured by BET (N_2 adsorption at -196 °C) using 150 sheets of the films. The surface area of 150 sheets of the bare glass plates was measured for corrections. The surface area of the calcined films thus obtained was as large as about 400 m^2/g, although it has been reported that niobia powders possessing high surface areas are hard to be prepared.5) Using a closed circulation system made of glass, the change in the surface area of the niobia films was monitored during the iterative adsorption (at 30 °C) and desorption (at 400 °C for 1 h) of water vapor. The results given in Fig. 2 show that no changes in the surface area of the films were observed even after 5 cycles of the iterative adsorption/desorption of water vapor. In Fig. 2 is also shown the change in the surface area of magnetite films, prepared from iron (III) nitrate dissolved in ethylene glycol, as mentioned in our previous paper.6) The surface area of the magnetite films significantly decreased with an increase in the number of the adsorption/desorption cycle. Consequently, the niobia films are proved to be extremely stable in the atmosphere of water vapor.

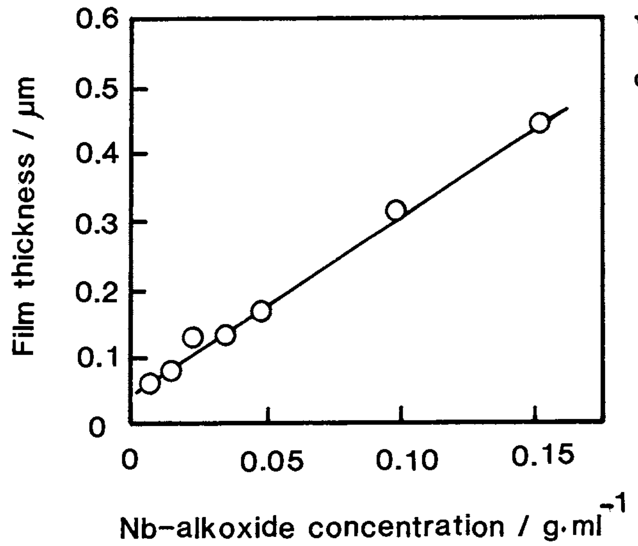

Fig. 1. Control of the film thickness by the concentration of Nb-alkoxide.

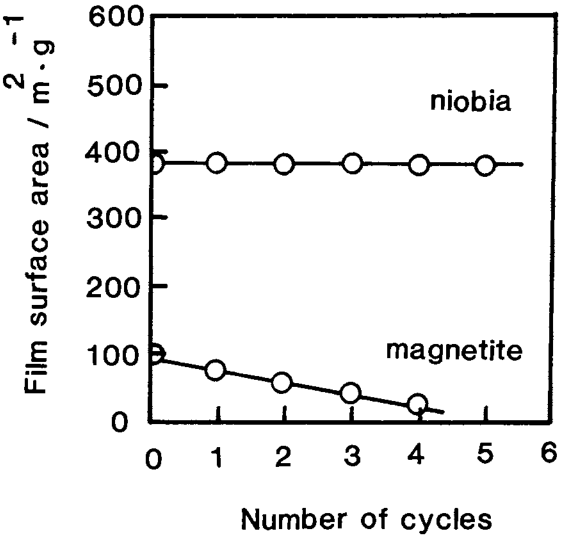

Fig. 2. Change in film surface area with adsorption/desorption cycles.

Changes in the electrical resistivity of the niobium oxide films, caused by adsorbed water, were measured by four-probe DC method with a current of 2 mA at room temperature. As is shown in Fig. 3, the electrical resistivity of the films in dry He atmosphere rapidly decreased immediately after an introduction of water vapor, corresponding to be 70% of the relative humidity. The resistivity was rapidly increased, conversely, when the water vapor was purged by dry He. An introduction of neither ethanol nor carbon dioxide over the oxide films affected on the resistivity of the films, leading to the conclusion that the niobia films are sensitive only to water vapor. Similar experiments were carried out on the magnetite films to be resulted in a significant sensitivity for both water vapor and ethanol.

As shown in Fig. 3, The film resistivity recovers to the original value, immediately after the water vapor was purged by dry He, while on the magnetite films it took a few minutes to recover the original resistivity. This will be attributed to a strong interaction between magnetite and water vapor adsorbed on it, resulting in an irreversible adsorption of water on the magnetite films. Thus, it is concluded that the niobium oxide thin films prepared here are of high durability for iterative adsorption/desorption cycles of water vapor, and of extremely high selectivity for water vapor adsorption.

In order to characterize the water vapor adsorbed on the films, changes in the impedance and the phase shift, caused by the adsorbed water, were measured by an LCR meter (Ando Denki Co., AG-4311) in the frequency range of 10 Hz to 100 kHz under various relative humidities. The oscillating frequencies lower than 100 Hz were supplied by an external synthesizer. The results obtained were converted to a complex impedance plot,[7)] yielding a semicircle, as shown in Fig. 4. Assuming

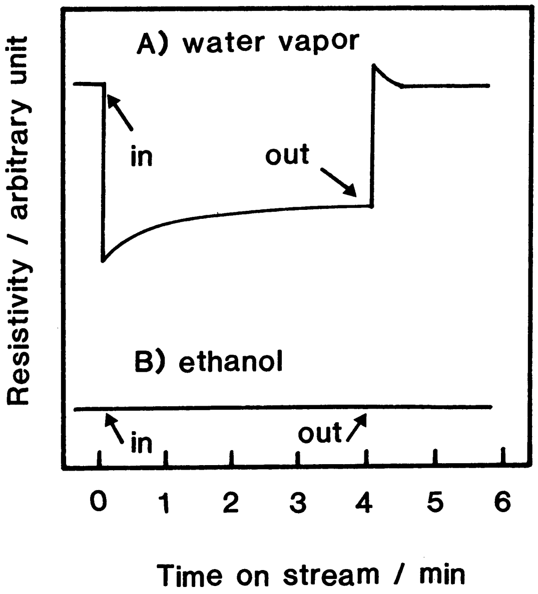

Fig.3. Change in the film resistivity.

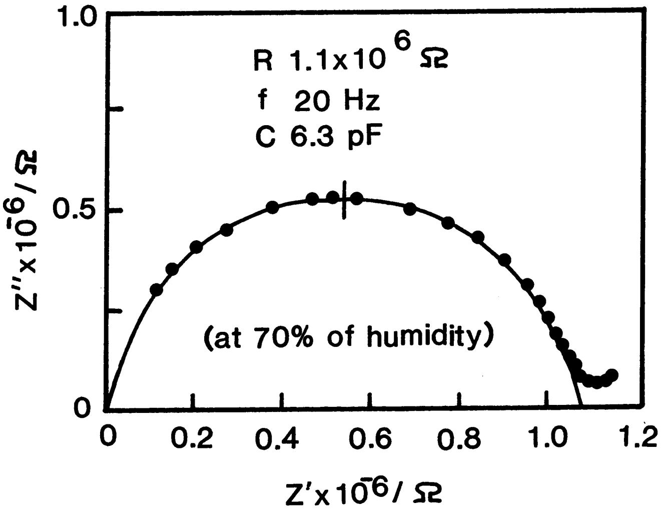

Fig.4. Complex impedance plot of niobia film.

an equivalent circuit (Fig. 5) for the niobia films adsorbing water, the circuit parameters such as resistance and capacitance of the films and the adsorbed water were calculated, respectively.[7] During the course of calculations, reciprocal of the film resistance(R_f) was neglected, because R_f is too large. Both the resistance and the capacitance calculated are plotted against the relative humidity, as depicted in Fig. 6. A constant capacitance at any humidities suggests the formation of, at most, monolayer adsorption of water vapor, since multilayer adsorption will lead to an enhanced capacitance. Water vapor thus adsorbed reacts with surface OH groups on the films to produce H_3O^+, which will be a charge carrier. Single semicircle shown in Fig. 4 indicates that either condensed water in micropores on the niobia films or water adsorbed on the smooth surface of the films is predominant, although it requests further studies to decide which is the case.

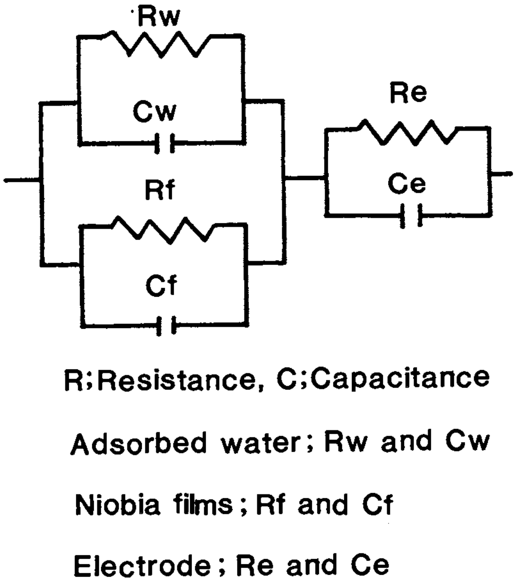

Fig. 5. Equivalent circuit of the niobia film adsorbed with water.

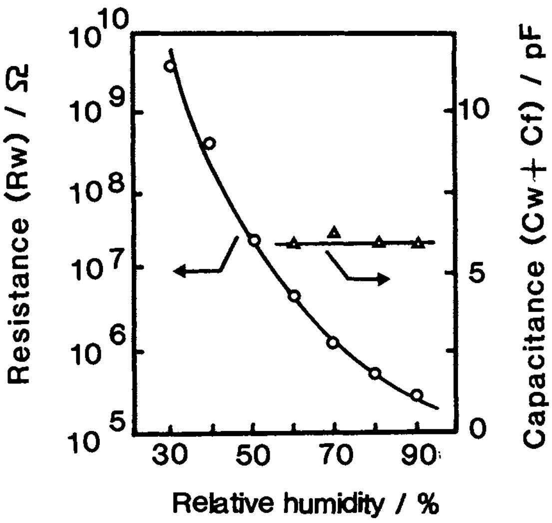

Fig. 6. Resistance and capacitance of equivalent circuit under various relative humidity.

The authors express their thanks to Prof. J.Kobayashi and Prof. Y.Morioka at Shizuoka University for LCR measurements and the data analyses.

References

1) T.Suzuki and N.Matsui, Proceedings of the International Meeting on Commercial Sensors, p.381, Kodansha(1983).
2) Y.Yokomizo, S.Uno, M.Harata, and H.Hiraki, Sensor Actuator, 4, 599(1983).
3) J.G.Weissman, E.I.Ko, and P.Wynblatt, J.Catal., 108, 383(1987).
4) T.Iizuka, K.Ogasawara, and K.Tanabe, Bull.Chem.Soc.Jpn., 56, 2927(1983).
5) S.Okazaki, Hyoumen, 27, 112(1989). (in japanese)
6) N.Takahashi, N.Kakuta, A.Ueno, K.Yamaguchi, and T.Fujii, Jpn.J.Appl.Phys., 28, L244(1989).
7) S.H.Chu and H.A.Seitz, J.Solid State Chem., 23, 297(1978).

(Received May 29, 1990)