Journal of Thermal Analysis, Vol. 40 (1993) 1193-1196

THERMAL ANALYSIS OF NICKEL OXIDE FILMS

P. Bukovec[1], *N. Bukovec*[1], *B. Orel*[2] *and K. S. Wissiak*[1]

[1]DEPARTMENT OF CHEMISTRY AND CHEMICAL TECHNOLOGY, UNIVERSITY OF LJUBLJANA
[2]INSTITUTE OF CHEMISTRY, 61000 LJUBLJANA, P.O.B. 537, SLOVENIA

Nickel oxide films were prepared by chemical deposition on glass substrates using nickel sulphate and potassium persulphate in ammonia solution. Coatings dried in air and at 85°C were characterized by thermal analysis (TG and DTG), FT-IR spectroscopy and X-ray diffraction. The films could be formulated as hydrated forms of $4Ni(OH)_2 \cdot NiOOH$ and $Ni_3O_2(OH)_4$ respectively. The coatings lost water and oxygen on heating to give NiO.

Keywords: nickel oxide films, semiconducting materials

Introduction

Nickel oxide is a semiconducting material extensively researched for its use in electrochromic coatings [1]. Nickel oxide films have usually been prepared by sputtering techniques [2] or by vacuum evaporation [3]. Only recently has a chemical method for the formation of nickel oxide thin films been reported [4]. Clean glass substrates were clamped vertically into a deposition mixture prepared from 1 *M* nickel sulphate, 0.25 *M* potassium persulphate and 14 *M* ammonia. After about one hour the glass was covered with a black deposit of NiO. The authors proposed the oxidation of Ni^{2+} to NiO_{1+x} in the first step and reduction by ammonia to NiO in the second step.

Nickel oxide used as anodic material in electrochromic coatings deposited electrochemically also appeared as NiOOH in brown or bronze colours [5, 6]. In the present investigation we tried to deposit nickel oxide films chemically with nickel in a higher oxidation state than two. The same method as already described [4] has been used, although with lower ammonia concentration.

Experimental

40 ml 1 *M* nickel sulphate and 30 ml 0.25 *M* potassium persulphate were poured together, and 22 ml 6 *M* ammonia added to this solution. Glass plates were fixed vertically in the prepared solutions and left there for 3–5 h. Brown to gray films deposited on the plates, which were then removed and washed with distilled

John Wiley & Sons, Limited, Chichester
Akadémiai Kiadó, Budapest

water and dried in the air for two days. Part of the sample was dried at 85°C for the same time.

Glass plates with nickel oxide films were placed into a powder diffractometer PW 1710 and spectra were recorded using CuK_{α_1} radiation ($\lambda = 1.54060$ Å). The films were also removed from the substrates and X-ray powder patterns of bulk material were taken with a Guinier de Wolff camera using CuK_{α_1} radiation and NaCl as an internal standard.

Table 1 X-ray powder patterns of $4Ni(OH)_2 \cdot NiOOH$, $Ni_3O_2(OH)_4$, and deposited air-dried and 85°C-dried nickel oxides

Nickel oxide film-air dried		$4Ni(OH)_2 \cdot NiOOH$	
d/Å	*I*	*d*/Å	*I*
7.80	100	7.70	100
4.40	40	–	–
4.00	20	–	–
3.85	90	3.85	80
3.10	20	–	–
2.55	90	2.56	80
2.40	30	–	–
2.30	80	2.31	80
2.20	10	–	–
1.87	80	–	–
1.74	10	1.75	10
1.52	30	1.53	80
1.49	40	1.50	80
1.19	20	–	–
Nickel oxide film dried at 85°C		$Ni_3O_2(OH)_4$	
d/Å	*I*	*d*/Å	*I*
4.70	100	4.70	100
4.00	80	–	–
3.10	50	–	–
2.65	90	2.63	10
2.60	20	–	–
2.45	40	2.42	80
1.54	50	1.52	50

Thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements were carried out using a Mettler TA 3000 modular system. Experimental conditions were: Pt crucibles, atmosphere of dry air with 30 ml/min flow rate, heating rate of 6 deg·min^{-1}. IR spectra were recorded on a Perkin Elmer FT-IR spectrometer 1721 X in the range 4000–220 cm^{-1}.

Results and discussion

X-ray powder patterns were compared with those in ASTM Data File [7] for various nickel oxides. The samples dried in air (bulk and films) corresponded to $4Ni(OH)_2·NiOOH$, although there were some additional lines in our samples (Table1) which could not be ascribed to known nickel oxides. The interplanar

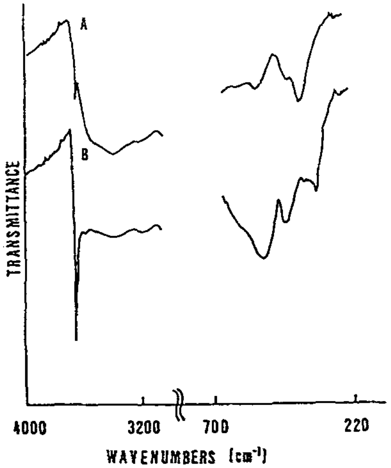

Fig. 1 FT-IR spectra of $4Ni(OH)_2·NiOOH·xH_2O$ (A), and $Ni_3O_2(OH)_4·xH_2O$ (B)

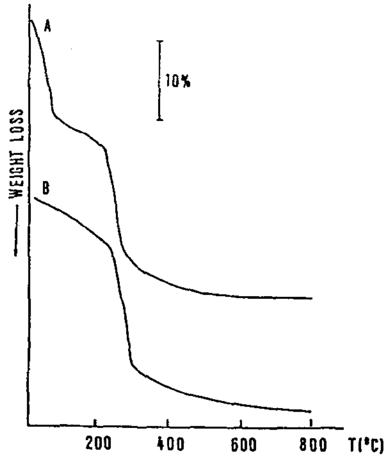

Fig. 2 TG curves of $4Ni(OH)_2·NiOOH·xH_2O$ (A) and $Ni_3O_2(OH)_4·xH_2O$ (B)

spacings of films and bulk material dried at 85°C showed the main lines of $Ni_3O_2(OH)_4$ (Table 1), again with some additional lines which did not correspond to any known nickel oxide. Some additional interplanar spacings were the same for both materials, e.g. 4.0, 3.1 Å.

FT-IR spectra of both materials are shown in Fig. 1. There are typical absorption bands for hydroxide stretching vibrations at 3638 cm^{-1} for samples dried in air, and 3640 cm^{-1} for samples dried at 85°C [8]. Apart from a broad H_2O stretching region and H_2O deformation, Ni–O stretching and probably H_2O librational absorption bands appear below 700 cm^{-1} [9, 10].

TG curves for both materials are shown in Fig 2. Loosely bound water in air-dried nickel oxide is released at low temperature. The next step, which begins at room temperature, can also be ascribed to loss of water as proved by decomposition of the substance dried at 85°C. The two dehydration processes overlap, although they can be ascribed to differently bonded water molecules. Above 200°C decomposition of hydroxide ions begins, giving off water molecules [11]. The final product of the decomposition is always NiO as proved by X-ray powder diffraction. This means that oxygen is also released in the final decomposition step due to the reduction of nickel.

Considering all the data, two materials could tentatively be formulated: $4Ni(OH)_2{\cdot}NiOOH{\cdot}5.78H_2O$ for air-dried and $Ni_3O_2(OH)_4{\cdot}1.53H_2O$ for 85°C-dried material respectively.

References

1 C. M. Lampert, Solar Energy Mater., 11 (1984) 27.
2 M. D. Rechtin and B. A. Averlach, J. Phys. Chem. Solids, 36 (1975) 893.
3 R. Tsu, L. Esaki and R. Ludeke, Phys. Rev. Lett., 23 (1969) 977.
4 P. Pramanik and S. Bhattacharya, J. Electrochem. Soc., 137 (1990) 3869.
5 S. Yamada, T. Yoshioka, M. Mayashita, K. Urabe, and M. Kitao, Optical Materials Technology for Energy Efficiency and Solar Energy Conversion VII, SPIE 1016 (1988) 34.
6 P. Delichere, S. Joiret and A. Hugot-Le Goff, Optical Materials Technology for Energy Efficiency and Solar Energy Conversion VII, SPIE 1016 (1988) 165.
7 Inorganic Index to the Powder Diffraction File 1967. Compiled under the Auspices of the Joint Committee on Powder Diffraction Standards. ASTM Publication PD 1S-17i.
8 H. Siebert, Anwendungen der Schwingungsspektroskopie in der Anorganischen Chemie, Springer Verlag, Berlin 1966, p.91.
9 J. R. Ferraro, Low-Frequency Vibrations of Inorganic and Coordination Compounds, Plenum Press, New York 1971, p.74.
10 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley Interscience, New York 1986.
11 R. C. Mackenzie and G. Berggren, Oxides and Hydroxides of Higher Valency Elements, in R. C. Mackenzie (Editor) Differential Thermal Analysis, AP London 1970, p.271.

Zusammenfassung — Dünnschichten aus Nickeloxid wurden durch chemische Abscheidung auf Glassubstraten mittels Nickelsulfat und Kaliumpersulfat in Ammoniaklösung hergestellt. Die in Luft und bei 85°C getrockneten Beschichtungen wurden dann mittels TG und DTG, FT-IR-Spektroskopie und Röntgendiffraktion charakterisiert. Diese Dünnschichten können als hydratierte Formen von $4Ni(OH)_2NiOOH$ und $Ni_3O_2(OH)_4$ beschrieben werden. Beim Erhitzen verlieren diese Beschichtungen Wasser und bilden NiO.