Journal of Thermal Analysis, Vol. 36 (1990)1063-1069

A DSC STUDY OF THE ETHYLCELLULOSE ADSORPTION ON SILVER POWDERS

*A. Heller** and *C. Fischer***

*DRESDEN UNIVERSITY OF TECHNOLOGY, DEPARTMENT OF CHEMISTRY,
MOMMSENSTR. 13, DDR-8027 DRESDEN**CENTRAL INSTITUTE OF SOLID STATE
PHYSICS AND MATERIALS RESEARCH, ACADEMY OF SCIENCES G.D.R.,
HELMHOLTZSTR. 20, DDR-8027 DRESDEN

(Received October 2, 1989)

DSC investigations reveal several bonding states of EC at the Ag surface. If O-bridged by alkoxide or carboxylic links EC is strongly adsorbed. If other tightly bonded species are present at the surface, the adsorption of EC is weak. Competitive adsorption and solvent efficiency cause a high adsorbance from EA and a low one from terpineol solution.

Adsorbed layers on powders applied in pastes for the screen printing process in hybrid microelectronics make a well-established contribution to the rheological behaviour. The present paper deals with the oxidation of adsorbed species on Ag powders to obtain information about their adsorbance and molecular state at the surface. To understand adsorption phenomena on Ag, its interaction with oxygen is of basic interest. Under ambient conditions, oxygen is adsorbed both molecularly ($O_{2,a}$) and dissociatively (O_a) [1]. Above 100° the adsorbed charged oxygen atoms become mobile.

Adsorption of alcohols and organic acids has been widely studied by ultra high vacuum analysis on Ag single crystal surfaces [2, 3]. Ag(110) is the most active face and represents a good model for polycrystalline materials. Without any population of O_a alcohols are only weakly adsorbed on Ag(110). In presence of O_a the elementary step of alcohol adsorption is connected with a proton transfer:

$$R{-}OH + O_a + = R{-}O_a + OH_a$$
$$R{-}OH + OH_a + = R{-}O_a + H_2O_a$$

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

This requires a well-situated location of O_a and an empty site (□).

Coverage and distribution of adsorbed oxygen atoms considerably affect sorption kinetics. The first stable product under ambient conditions should be a carboxylate, unless the oxidation of alkoxides is a hindered process. Other than by oxidation, adsorbed alkoxides and carboxylates may disappear from the surface by displacement with stronger acids (4):

$$R^1\text{–}O_a + R^2\text{–}OH = R^1\text{–}OH + R^2\text{–}O_a$$

Experimental

Two types of Ag powders were selected for this study:

1. a commercial product (Ag(E) prepared by reduction of Ag_2CO_3 with hydrazine in alkaline aqueous solution; BET surface 1.74 m^2/g.

2. a powder, prepared from Ag_2CO_3 by reduction with ethylene glycol at 100° (Ag(U); BET surface 0.26 m^2/g [4].

Adsorption measurements were carried out using 50 mg samples immersed in 5 ml solution. For dispersion and to establish equilibrium the system was rotated at low rate in inclined centrifuge tubes for 16 h. After subsequent centrifugation the solution was poured out and the powder was washed 3 times with 5 ml acetone, then vacuum dried at 30°. All DSC runs (Perkin Elmer DSC-4) were carried out in air at the rate of 10 deg.min^{-1} with sample weights of 10 mg. The Hercules type ethylcellulose N300 (EC) was used without further purification. The applied solvents were commercial ethyl acetate (p.a. Chemapol) (EA) and terpineol, redistilled in a rotary vacuum evaporator at 7 kPa.

Results and discussion

Both Ag powders are well characterized by DSC traces (Fig. 1). The narrow shape of the peaks indicates a vigorous oxidation of adsorbed species. A drastic acceleration taking place after an activation step has been overcome. These results confirm the assumption that the dissociative adsorption of oxygen on the surface is hindered at full coverage by alkoxide or carboxylate. After the adsorbed O-bases have become mobile, dissociative adsorption of oxygen occurs and oxidation starts. Water formed during the reaction desorbs easily and provides new sites for the O_a pathway. The O_a-coverage rises rapidly and oxidation proceeds with increasing rate. To interpret the different peak temperatures, some experiments were performed. Ag powder was treated with a series of alcohol-EA-mixtures for 16 h a) in its initial state and b) after combustion of the surface adsorbate by heating up in air to 190°. Figures 2 and 3 show the obtained DSC traces.

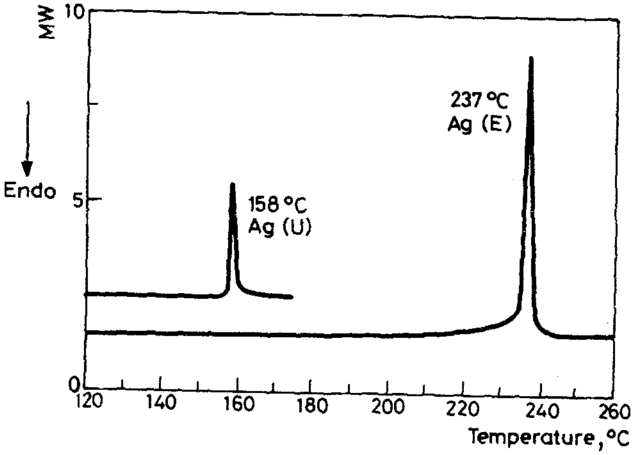

Fig. 1 DSC curves of the powders Ag(U) and Ag(E)

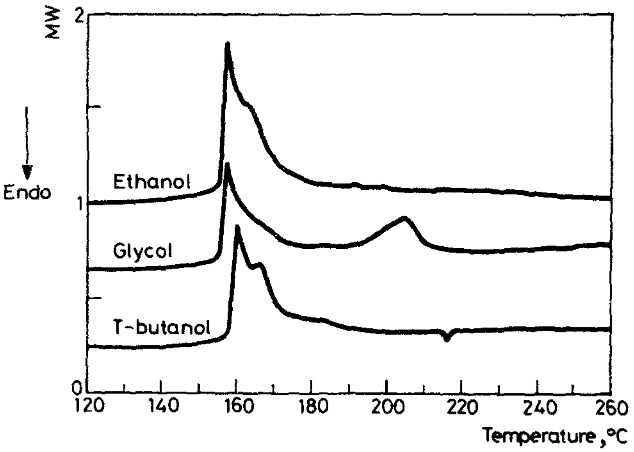

Fig. 2 DSC curves of the Ag(U) powder treated for 16 h with alcohol/EA (1:99) mixtures

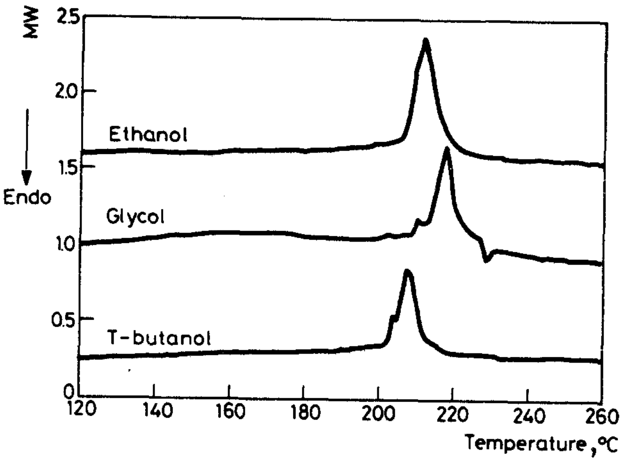

Fig. 3 DSC curves of the preoxidized Ag(U) powder treated for 16 h with alcohol/EA (1:99) mixtures

In the first case, only a weak effect is detected. It appears that, due to their similar acidity, alcohols do not drastically change the initial peak which is supposed to arise from a glycolate (Ag(U)). After combustion of the organic material and adsorption of alcohols on the oxygen covered surface the DSC peaks were shifted upward by about 50°.

Table 1 Peak temperatures of the adsorbate oxidation of Ag(U) powder

Mixture for adsorption	Mixture ratio	T_{peak}, °C	
		On initial surface	On preoxid surface
	–	158	-
Methanol/EA	1:99	159	207
Ethanol/EA	1:99	158	211
t-Butanol/EA	1:99	160	207
Glycol/EA	1:99	158(205)	218
Terpineol	–	205	
Acetic acid/EA	1:99	215	214
Oleic acid/Ethanol	1:99	242	
EC/EA	2.1 g/l	168(195)	196

It was concluded that carboxylates or, in the case of t-butanol, a stable alkoxide were formed [5]. This conclusion is supported by the fact, that the initial peak of the Ag(U) - sample is shifted by treatment with acetic acid to about the same extent. This is in accordance with the result, that adsorbed alkoxides are displaced by stronger acidic species [6].

Screening of molecular oxygen from the surface like in the case of oleic acid yields a striking effect on the peak location. The adsorption of EC on

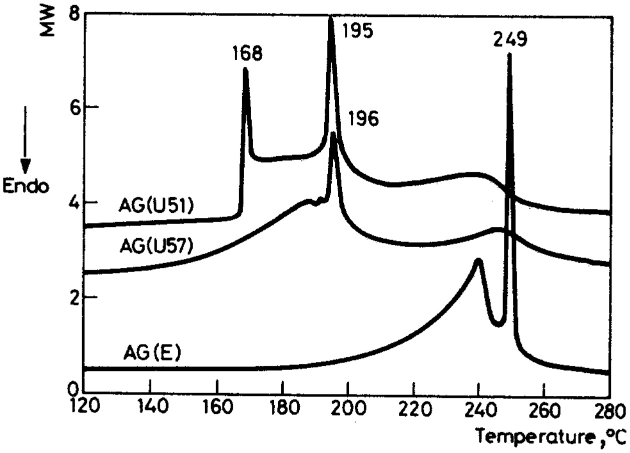

Fig. 4 DSC curves of Ag powders treated with EC/EA solution (2.1 g/l). Ag(U51) – initial powder; Ag(U57) – preoxidized powder

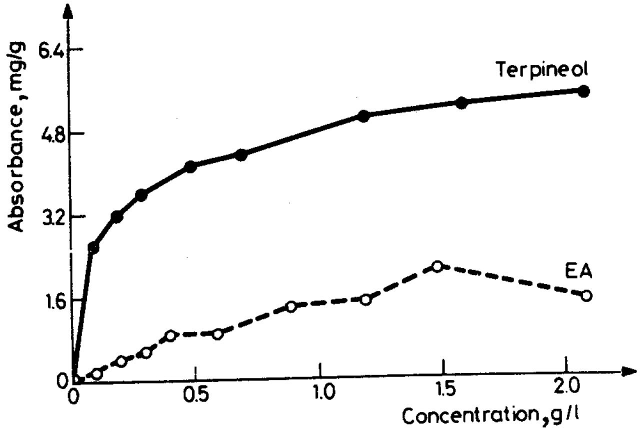

Fig. 5 Isotherms of EC adsorption at the Ag(E) powder from terpineol and EA solution; T = 20 °C

Ag(U) powder, as prepared and preoxidized at 190° in air was examined, too. In the case of preoxidized samples, three peaks of the recorded DSC curve could be distinguished (Fig. 4):

– A narrow peak appears at 196°. It is assigned to the oxidation of a sterically hindered alkoxide, which arises from the reaction at the non-esterified OH or from the oxidation at a carboxylic link to the cellulose chain.

– Two broad peaks are located at 185° and 245°, which were also found in the bulk oxidation of EC. However, the first peak is not always present (Fig. 5). It may be suppressed or promoted due to adsorption. The influence may be thought of a conformational constraint or catalytic effects.

– The peak at 245° almost approaches the main peak from the bulk oxidation. We concluded, that a catalytic influence is diminished in this case. The peak may be mainly caused by tails and loops of the adsorbed polymer chain, because they are not in direct contact with the Ag surface.

The sample without preoxidation shows additionally the peak of the initial powder. This indicates that the EC only partially displaces the primary glycolate. The DSC curve of the Ag(E) sample bearing adsorbed EC shows a similar feature. The initial narrow peak at 249° is retained. The primary adsorbate related to that peak builds up a screening layer which allows only a weak bonding to the EC molecules. This will be evident, too, comparing the weight losses owing to washing the Ag(U) and AG(E) samples with acetone after the EC sorption. The weakly adsorbed EC on Ag(E) is gradually removed, contrary to the EC on the Ag(U).

Table 2 Effect of washing on the adsorbance of EC

Number of washing processes		1	3	5	7
Adsorbance, mg/g	Ag(U)	3.14	3.44	3.41	3.46
	Ag((E)	5.73	4.87	4.28	3.99

The adsorption isotherms of EC on Ag(E) from EA and terpineol solutions basing upon the measurements of heat of oxidation (h) are given in Fig. 5. The calibration of h by weight loss (m) of the sample fits the equation $h/\mathrm{J} = 12.6\ m/\mathrm{mg}$). The narrow peak not attributed to EC-oxidation on this powder was excluded.

It is immediately evident that a strong adsorption takes place from EA solution but a weak one from terpineol solution. Regarding the competition between solvent and EC the terpineol makes a contribution to adsorption, whereas EA shows no affinity to the surface.

In addition to the interaction energy the efficiency of the solvent plays a dominant role. The better solvent properties of terpineol for EC [7] prevent an enhanced concentration of EC at the surface. In the EA solution a strong increase of adsorbed amount is observed already at low concentration, as it is typical for polymers [8]. The coverage at saturation is estimated to 2.4 mg/m^2 in EA solution and to 0.9 mg/m^2 in terpineol solution.

References

1 A. W.Czanderna, J. Phys. Chem., 68 (1964) 2765.
2 I. E. Wachs and R. J. Madix, Appl. Surf. Sci., 1 (1978) 303.
3 A. G. Sault and R. J. Madix, Surf. Sci., 172 (1986) 598.
4 C. Fischer and A. Heller, Mat. Research Bull., 24 (1989) No.10.
5 R. L. Brainard and R. J. Madix, J. Am. Chem. Soc., 109 (1987) 8082.
6 M. A. Barteau and R. J. Madix, Surf. Sci., 120 (1982) 262.
7 R. M. Stanton, J. Hybrid Microelectronics, 6 (1983) 419.
8 B. E. Platonov, T. E. Saloveva and W. M. Kaljushny, Ukrainski Chim. J., 50 (1984) 1143.

Zusammenfassung — Durch DSC Aufnahmen können verschiedene Bindungszustande von EC an Ag Oberflächen nachgewiesen werden. Über O-Brücken als Alkoxid oder Carboxylat gebundene EC ist fest sorbiert. Bei Vorhandensein anderer fest gebundener Species tritt nur eine schwache Sorption auf. Konkurrenzadsorption und Güte des Lösungsmittels führen zu einer hohen Adsorption aus EA- und einer niedrigen aus Terpineol-Lösung.