Thermochimica Acta, 29 (1979) 333–337
© Elsevier Scientific Publishing Company, Amsterdam – Printed in the Netherlands

AES, WORK FUNCTION AND GRAVIMETRIC MEASUREMENTS OF THE OXYGEN INTERACTION WITH Al AND Cu FILM SURFACES

C. BENNDORF, B. EGERT, H. SEIDEL and F. THIEME
Institut für Physikalische Chemie der Universität Hamburg,
Laufgraben 24, 2 Hamburg 13, Germany

ABSTRACT

The interaction of oxygen with Al and Cu films was investigated by means of gravimetric uptake, Auger electron spectroscopy (AES) and work function changes. For Al it was possible to separate two reaction rates, a logarithmic one for an oxygen uptake $< 6\times10^{-8}$ g/cm^2 with only a slight decrease of the reaction rate and an inverse logarithmic one for mass uptake $> 8\times10^{-8}$ g/cm^2. The interaction of Cu films with oxygen is characterized by a drastic decrease of the sticking coefficient from the very beginning of exposure. The maximum mass gain attainable at 7×10^5 L with 4×10^{-8} g/cm^2 is evidently below a dissociative one monolayer coverage. From the AES, ELS and work function measurements we could prove the growing of aluminum oxide from the very beginning of oxygen interaction. Contrary, on evaporated Cu films no significant changes in the Auger line shape and the energy loss spectra were detected up to an exposure of 7×10^5 L. This stage of oxygen interaction with Cu is described as chemisorption.

INTRODUCTION

The aim of this paper is to demonstrate the usefulness of gravimetric measurements in correlation with surface specific methods as AES and work function changes in the initial stage of oxygen interaction with evaporated Al and Cu film surfaces.

EXPERIMENTAL

The experiments were performed in a conventional stainless steel

UHV system with base pressure below $1x10^{-10}$ Torr. Aluminum was evaporated from a small electron beam evaporator /1/ (copper from a Ta helix) onto the working crystal of the microbalance and at the same time onto a glass substrate mounted on the heatable and coolable manipulator. The changes on the substrate film during oxygen interaction could be followed by AES, ELS or work function measurements and quasi simultaneous the mass gain was measured with the quartz microbalance /2/.

The quartz microbalance assembly is shown in Fig.1. Two piezoelectric quartz crystals with frequencies of 4.88 MHz were mounted on

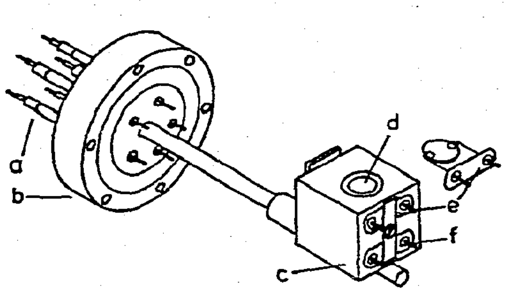

Fig.1. Quartz crystal holder
(a)-electrical feedthroughs
(b)-38-mm-i.d.-flange
(c)-adjustable crystal holder
(d)-aperture for evaporation
(e)-working quartz
(f)-reference quartz

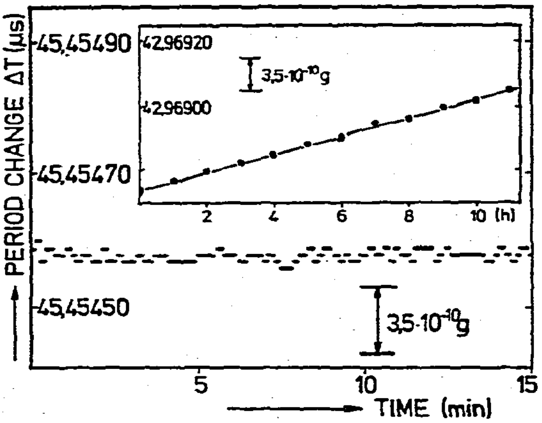

Fig.2. Noise level of the quartz oscillator microbalance
Inset: long time stability

ground plates conventional in rf-technique. Temperature was stabilized by a surrounding stainless steel block open only for the working quartz, the second crystal serving as reference. A simple oscillator circuit without any inductivities was used. We measured the period difference ΔT_{12} with a counter with a resolution of 10^{-11}s. During the experiments reported here we had ΔT_{12} = 45 µs and thus a resolution of $\Delta m = 3.5x10^{-11}$g /2/. This high resolution with an excellent long time stability is only slightly affected by a certain noise level (Fig.2).

RESULTS

Initial oxidation of aluminum

The oxygen mass uptake as function of exposure (O_2 pressure $1x10^{-6}$ Torr) during the oxidation of aluminum is shown in Fig.3. At the beginning a relative fast rate with a sticking coefficient of 3×10^{-2} was found. A drastic decrease of the sticking coefficient was measured at dosages 10^3 L corresponding to a mass gain of 7×10^{-8}g/cm^2. This

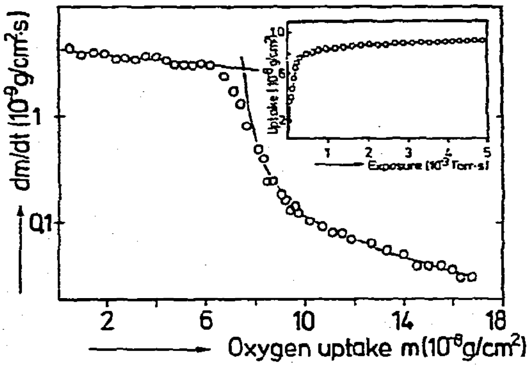

Fig.3. Logarithmic reaction rate of Al against oxygen uptake. Inset: Oxygen uptake as function of exposure

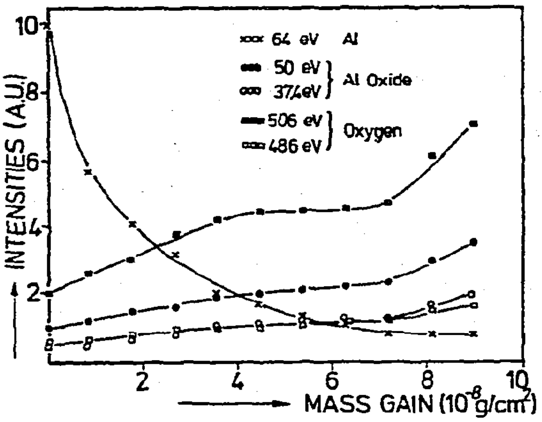

Fig.4. Peak to peak heights of the AES intensities of the 64, 50, 37.5 eV Al and the 506 and 486 eV oxygen lines against oxygen uptake.

change of reaction rate is seen more pronounced by a plot of the logarithmic reaction rate ln(dm/dt) against mass Δm /3/. In order to illustrate the measured values we calculated the mass of a dissociative oxygen monolayer on a smooth single crystal surface. Assuming an equal distribution of the three main crystallographic surfaces in the aluminum film we obtained 2.8×10^{-8}g/cm^2. Even supposing a great surface roughness of the evaporated films this calculated value is much below the experimental result of $\Delta m = 9\times10^{-8}$g/cm^2, which marked the drastic decrease of the sticking coefficient.

Drastic changes in the low energy $L_{23}VV$ Auger line shape were observed from the very beginning of oxygen exposure. The two new lines at 37.5 and 50 eV could be attributed to cross transitions involving oxygen induced 2p and 2s levels /3,4/. The intensities determined by the peak to peak height of the derivative dN/dE of these new lines at 37.5 and 50 eV of the Al($L_{23}VV$) and the oxygen (KLL) lines against the mass gain are plotted in Fig.4. Surprisingly, the intensity of the oxygen peak does not grow linearly with the oxygen uptake m. The change from the flat part to a growing intensity coincide with the drastic decrease of the sticking coefficient. The Al 64 eV Auger line as well does not obey the supposed rate law, an exponential decay due to the small escape depth of the low energy electrons. Certainly, the behaviour of the low energy Al lines is somewhat obscured by the drastic changes in the band structure during oxidation.

Oxygen interaction with Cu

The results of the initial interaction of oxygen with evaporated Cu films are very different from the behaviour we measured on aluminum. While the sticking coefficient at zero coverage with values about 10^{-1} is comparable with Al, a drastic decrease of the adsorption rate is found even for very low mass uptake. The maximum exposure of 7×10^{5} L resulted in a mass gain of only 4.1×10^{-8} g/cm^2. Assuming a surface roughness of 1.8 and an equal distribution of the main crystallographic surfaces in the film surface we obtain for the dissociative one monolayer coverage a mass of 6.5×10^{-8} g/cm^2, which is evident above the experimental result of 4.1×10^{-8} g/cm^2 (Fig.5) /5/.

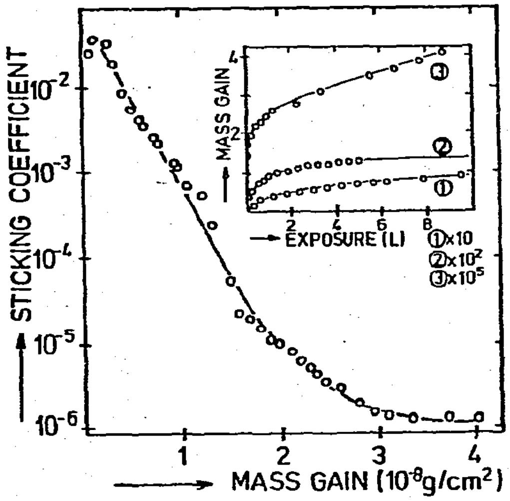

Fig.5. Sticking coefficient of Cu as function of oxygen mass gain.
Inset: Mass gain (10^{-8} g/cm^2) against oxygen exposure. The curves 1, 2, 3 correspond to a full scale of 10^2, 10^3 or 10^6 L, respectively.

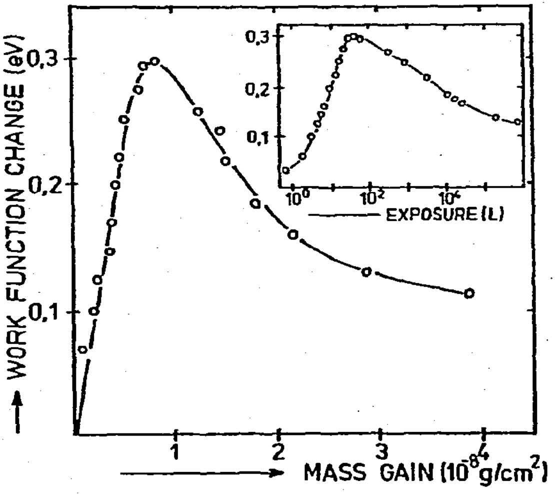

Fig.6. Work function change as function of oxygen mass gain. Inset: Work function change against oxygen exposure.

The work function changes of the Cu film during oxygen exposure (Fig.6) can be interpreted in terms of two states of chemisorbed oxygen. In the beginning an increase of $\Delta\phi$ with a maximum value of 0.3 eV at about 70 L -corresponding to a mass gain of 0.8×10^{-8} g/cm^2- was found. A second state of adsorbed oxygen with a decrease of work function was observed at higher oxygen exposures. The initial increase of $\Delta\phi$ is in agreement with the measurements of DELCHAR /6/ and HOFMANN et al. /7/. The interpretation of the initial increase of $\Delta\phi$ is similar to the corresponding results on Al at low temperatures /3/. The decrease of work function at higher oxygen exposure, which was found recently by HOFMANN et al. /7/ on Cu(100) too, is probably due to a reconstruction or incorporation. But this process is not equivalent to the formation of any copper oxide as we confirmed by ELS /8/.

ACKNOWLEDGEMENT

We thank the "Deutsche Forschungsgemeinschaft" for financial support.

REFERENCES

1 C.Benndorf, H.Seidel, F. Thieme, Rev.Sci.Instrum., 47(1976)778
2 C.Benndorf, H.Seidel, F. Thieme, J.Vac.Sci.Technol., 14(1977)819
3 C.Benndorf, H.Seidel, F. Thieme, Surface Sci., 67(1977)469
4 P.H.Citrin, J.E.Rowe, S.B.Christman, Phys.Rev., B14(1976)2642
5 C.Benndorf, B.Egert, G.Keller, H.Seidel, F.Thieme, J.Vac.Sci.Technol., in press
6 T.A.Delchar, Surface Sci., 27(1971)11
7 P.Hofmann, R.Unwin, W.Wyrobisch, A.M.Bradshaw, Surface Sci., 72 (1978)635
8 C.Benndorf, B.Egert, G.Keller, F.Thieme, Surface Sci.,74(1978)216