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SURFACE DIFFUSION OF LITHIUM ON THE W(112) PLANE BY FIELD EMISSION SPECTRAL DENSITY ANALYSIS

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Abstract - The spectral density functions $W(f)$ of the field-emission flicker noise of lithium adsorbed on the tungsten (112) plane were determined at different temperatures in a probe-hole field emission microscope. By an analysis in terms of the Timm and van der Ziel model the surface diffusion coefficients have been obtained and their temperature dependence reveals the surface diffusion energies. For the two coverages of $c = 0.38$ and $0.75$ investigated their values could be determined to be $Q = 0.56$ and $1.08$ eV respectively. The diffusivity prefactors were also calculated. The results are compared with those obtained for the W(112)K system.

1 - INTRODUCTION

Alkali metal adsorption on metals is a subject of long-standing and current interest /1/ and much effort has been made with different surface spectroscopies to investigate its properties. Surface diffusion is important for many processes but only a few parameters were obtained for lithium on single planes on transition metals /2,3/. The flicker noise or fluctuation methods /3,4/ are advantageous in allowing easily to determine the coverage and even the directional dependence /5,6/ though a certain polarization contribution by the high voltage needed is unavoidable. From potassium investigations we know of a strong effect of the coverage /7/ and of surface structure /8/. Noise measurements of the spectral density in dependence on coverage of the same W(112)Li system /9/ show clearly the influence of coherent and incoherent adlayer structures on the adatom mobility. The results presented here illustrate the applicability of the technique but can give only an example of the surface diffusion parameters for two selected coverages.

2 - EXPERIMENTAL

A field emission microscope (FEM) of the Müller probe-hole type was used to measure the current fluctuations from the central part of the (112) plane of a tungsten single crystal tip covered with a lithium submonolayer. The lithium source consisted of a Li zeolite placed on a resistively heated tantalum sheet. The temperature of the emitter was kept constant by means of a stabilized emitter loop current which was calibrated earlier.

The field emission current was analysed between 25 Hz and 20 kHz by a frequency spectrometer (Echtzeitanalyzer 01012, Messelektronik, Dresden). More experimental details can be found in ref. /9/.

The flicker noise spectral density functions $W(f)$ were measured in dependence on temperature (above room temperature) for some Li concentrations. The chosen coverages were obtained by heating the emitter covered with a thick layer of lithium —i.e. by thermal desorption of Li from the W(112) plane. The coverages were determined by measuring the voltage at a constant collector current from the W(112) plane with and without lithium. This allows to calculate the work function, and we obtain the adsorbate...
concentration by taking into account the dependence of the work function
versus lithium deposition doses which was calibrated by the concentration
ratio $c = n_{Li}/n_{WC}$, in ref. 2 (see also ref. 9).

3 - RESULTS

The temperature dependence of the spectral density function is illustrated
in figs. 1 and 2 which correspond to $c = 0.75$ and $0.38$, respectively. (Other
spectra at intermediate temperatures and the same coverages not shown here
fit well into the general trend to be described below.) The increase of the
emitter temperature leads to a change of the $W(f)$ shape in the investigated
frequency range. At room temperature (and slightly above) $W(f)$ can be
represented by one straight line in a double logarithmic scale and described
by the equation $W(f) \propto f^{-2}$ (figs. 1a, b, 2a).

![Fig. 1 - Experimental spectral density functions at different temperatures for
$c = 0.75$ (circles). Except for the curves at $T = 378$ K and $450$ K, the
experimental points are fitted by theoretical curves of the Timm and van der
Ziel model.](image)
Fig. 2. Experimental spectral density functions at different temperatures for $c = 0.38$ (circles). Except for the curve at $T = 378$ K, the experimental points are fitted by theoretical curves of the Timm and van der Ziel model.
For the higher temperatures the experimental points are approximated by the theoretical spectral density function obtained by Timm and van der Ziei [10] and corrected by Gesley and Swanson [11]. These authors have assumed a model where surface diffusion of the adsorbate on a small circular probe area causes fluctuations in the number of adparticles on this area. The fluctuations are described by the spectral density function $S(u)$ given by

$$S(u) = C_{FN} \langle \delta N_i^2 \rangle p \, \frac{r_p^2}{D} \, T(u),$$

where $u = 2n \pi r^2 / D$ is the normalized frequency and $T(u)$ an expression composed of Kelvin functions ($C_p/6$), $\langle \delta N_i^2 \rangle$ is the mean-square fluctuation of the adparticle number on the probed area with radius $r_p$, $D$ is the surface diffusion coefficient and $C_{FN}$ the Fowler-Nordheim term.

The temperature above which the change of the $W(f)$ shape can be observed depends on the lithium coverage. For example at the high concentration of $c \approx 2.45$ a temperature increase above room temperature leads already to a decrease of the lithium concentration on the W(112) plane (according to the voltage at constant collector current). At a temperature of about 504 K $c$ approaches unity. A visible change of the $W(f)$ shape took place for $c = 0.75$ and $c = 0.38$ at $T = 460$ K and $T = 400$ K, respectively.

4 - EVALUATION AND DISCUSSION

By comparing the experimental spectral density function $W(f)$ with theory the diffusion coefficient has been calculated. As it was done in ref. [7] for the W-K system the frequency scales that correspond to the experimental $W(f)$ (lower scale in figs. 1 and 2) were compared with the frequency scale that corresponds to the dimensionless normalized "frequency" $u_p$ defined above (upper scale). From this comparison and taking the probed area radius to be about $10^{-8}$ cm the diffusion coefficient $D$ can be obtained. Figs. 3 and 4 illustrate its temperature dependence for the $W(f)$ examples shown in figs. 1 and 2, respectively. The data is well represented by a straight line fit.

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Fig. 3 - Arrhenius plot of the diffusion coefficients at a concentration of $c = 0.75$ ($Q = 1.08$ eV).

Fig. 4 - Arrhenius plot of the diffusion coefficients at a concentration of $c = 0.38$ ($Q = 0.56$ eV).
From the Arrhenius plots of the diffusion coefficients we have the surface diffusion activation energy $Q = 0.56$ eV and the prefactor $D_0 = 2.4 \times 10^{-3} \text{cm}^2/\text{s}$ at the Li concentration of $c = 0.38$. At the higher coverage ($c = 0.75$), the respective values are considerably higher: $Q = 1.08$ eV and $D_0 = 6.3 \times 10^{-4} \text{cm}^2/\text{s}$.

The Li activation energies are in general larger than those for potassium on the W(112) plane /7/ which appears to be a natural consequence of the smaller size of Li atoms or ions. (This is not true, however, for the first value of $Q = 0.56$ eV at a coverage where $Q$ was found to be somewhat higher /7/). A detailed comparison requires more Li data especially at different coverages than are available at present.

According to figs. 1 and 2 the experimental spectral density functions are fitted rather well by the theoretical curves of the Timm and van der Ziel model ($S_\infty$) except in the lower temperature range. There $W(f)$ can be described by the spectrum $W(f) \propto f^{-\alpha}$ which reveals a straight line in a double logarithmic plot. With increasing temperature small discrepancies develop at the high frequency part of the measured spectra (only a part of them is shown in figs. 1 and 2). Finally the curves of the two-dimensional (2D) fluctuation model $S_\infty$ (cf. /11/) describe the spectra as mentioned above. It seems that this temperature dependence can be explained in the following way: Near room temperature we observe in fact a one-dimensional diffusion along the rows of the bcc (112) plane of tungsten. The adequate 1D-model gives the spectrum $S_{1D}$ derived by Gesley and Swanson /11/. This function plotted in fig.1 of ref. /11/ versus the normalized frequency $u = \omega r^2 / D$ is not exactly a straight line but can be approximated for, say, $1/2$ or $2$ frequency decades by straight lines with a slope between $\alpha = 1$ and $1.5$. Considering the approximate description of the real diffusion by the 1D-model one can in fact explain the spectra by these arguments.

At higher temperatures, however, we find some deviations at low frequencies (fig. 2h) and another mechanism might be responsible for them. We expect a phase transition from the ordered phase to the disordered but the theories developed so far disregard this transition. The beginning of an observable substrate atom mobility might also show up at these temperatures /12/.

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**Fig. 5** - Spectral densities $W(f)$ versus reciprocal temperature for a concentration of $c = 0.75$.

**Fig. 6** - Spectral densities $W(f)$ versus reciprocal temperature for a concentration of $c = 0.38$. 
The temperature dependence of the spectral densities (figs. 5 and 6) reflects the general trend of the complete spectra: with rising temperature the noise power also increases but we have at the same time diminishing low frequency parts of the W(f)'s according to the change from the 1D- to the 2D-spectra, namely $S_{1D}$ changing to $S_{2D}$. Therefore, at the coverage of $c = 0.38$ (fig. 6) we observe at first a $W(1 \text{ kHz})$ maximum followed by the $W(10 \text{ kHz})$ maximum. A similar behaviour at $c = 0.75$ (fig. 5) is expected at higher temperatures because of the following reason. From the Arrhenius plots of the diffusion coefficients we found the surface diffusion activation energy $Q = 0.56$ and $1.08 \text{ eV}$ at the Li concentration of $c = 0.38$ and $0.75$ respectively. Therefore one expects in fact the maximum of fig. 5 at higher temperatures.

It is interesting to note that a similar dependence of the spectral densities with reciprocal temperature was observed also for clean /12/ and heavily covered /13/ tungsten tips as well as for epitaxial K crystals /14/. The lithium investigations and their interpretation in terms of surface diffusion presented above may also explain the general fluctuation behaviour of the three mentioned surfaces (cp also /15/) if the number of mobile atoms is not too large.

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