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Spectral density of elastically backscattered electrons from Pd(110) covered with segregated sulfur

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A partial segregated sulfur coverage on Pd(110) plane has been obtained by heating the sample. The segregation has been investigated and the state of the palladium surface has been monitored by means of Auger electron spectroscopy. The temperature and the segregation energy have been estimated. The intensity fluctuations of the elastically backscattered electrons (for primary energy $E_p = 300$ eV) from the surface, prepared in such way, have been investigated. The intensity fluctuations of the elastically backscattered electrons have been quantitatively described by the power spectral density functions. The power of the low-frequency fluctuations (from 6 to 10 Hz) has shown an increase with increasing sample temperature. The fluctuations are interpreted as resulting from local-density fluctuations of an adsorbate. The diffusion activation energies have been estimated. [S0163-1829(99)08127-8]

I. INTRODUCTION

Experimental results on surface diffusion and surface segregation of sulfur on palladium (110) are presented. The diffusion results have been obtained by measurements of current fluctuations of the elastically backscattered electrons from a palladium specimen covered with sulfur, versus temperature. The current fluctuation of the backscattered electrons are quantitatively described with a spectral density function, commonly used in a description of field-emission flicker noise. Similarly to the case of field emission, e.g., Refs. 1–3, or the recently described case of scanning tunneling microscopy (STM) tunneling current,[4] these fluctuations are interpreted as resulting from the local-density fluctuations of an adsorbate. However, the spectral density functions for elastically backscattered electrons differ significantly from those mentioned above, and show thermally induced changes for a certain frequency range only. This was previously observed for polycrystalline titanium covered with sulfur.[5]

II. EXPERIMENT AND DATA PROCESSING

The measurements were performed in a stainless-steel UHV system at a base pressure of 7×10^{-8} Pa. The palladium (110) specimen was mechanically and chemically polished and mounted on a rotable manipulator. It was cleaned by a potassium ion bombardment (ion energy 1500 eV, ion current 2 μA) together with a heat treatment. During the cleaning the sample temperature of 800 K was maintained to prevent potassium ions from adsorption. The heating of the sample, from room temperature up to 1000 K, led to the segregation of sulfur onto the surface, so that the sulfur Auger peak height became greater than that of palladium. The thermal segregation of the sulfur (and, on the other hand, the ion bombardment) has made it possible to control (to a certain extent) the sulfur coverage of the palladium surface. Some amount of phosphorus was present in the bulk. After subsequent cycles of heating, its cosegregation onto the surface of the sample was also observed.

Spectra of the elastically backscattered electrons and Auger electrons were recorded with a cylindrical mirror analyzer (CMA) described elsewhere.[6] The current of the elastically backscattered electrons was measured via a CMA spectrometer at the pass energy (equal to the incident electron energy) of 300 eV. The current fluctuations have been measured in a frequency range from 1.5 up to 500 Hz, and registered by a computer using an analog-to-digital converter. The single measurement consisted of 15 000 samples at a 1-kHz sampling frequency. The power spectral density functions were subsequently calculated as the square modules of the discrete Fourier transforms (FFT) of the signals. The power of fluctuations in a particular frequency range was obtained via integration of the spectral density function over this range. The temperature was maintained constant (within ±5 K) during each measurement, and changed stepwise in the range from 300 up to 625 K in a whole series. The time between the measurements in the series was approximately 60 s. After each series of measurements for increasing and decreasing temperature, a single measurement of the apparatus induced noise was made in order to estimate the experimental error.

III. RESULTS AND DISCUSSION

The segregation of sulfur onto Pd(110) surface was investigated via measurements of the relative Auger peak heights with increasing temperature. In Fig. 1 the ratio of the S Auger peak at 152 eV to the Pd peak at 327 eV is plotted in a semilogarithmic scale versus the reciprocal of the sample temperature. For temperatures above 700 K (corresponding to the point $\approx 1.43\times10^{-3}\text{K}^{-1}$) a linear approximation can be made with a good correlation coefficient $\rho\approx-0.97$. Assuming that for these temperatures T the Auger peak height ratio $\propto e^{-E_s/k_BT}$ (k_B is the Boltzmann constant), the segregation energy $E_s = 310\pm20$ meV per atom was found from the slope of the regression line. This value does not differ significantly from the segregation energy 180 ± 40 meV, which was calculated for polycrystalline palladium using data (surface composition vs temperature) taken from Ref. 7.

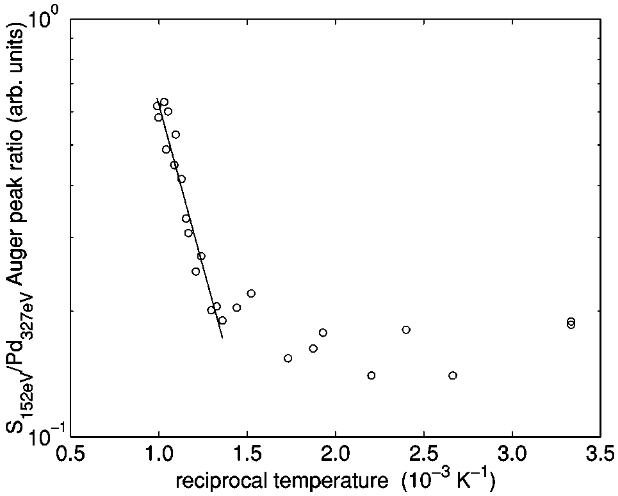

FIG. 1. The dependency of the S/Pd Auger peak ratio on the reciprocal of Pd(110) surface temperature.

The obtained segregation temperature 700 K is in a good agreement with temperatures observed previously for other palladium planes [e.g., Pd(100) (Refs. 8 and 9) and Pd(111) (Ref. 10)]. The measured value of E_s is lower than found for sulfur segregation on other metals, e.g., nickel[11] or tungsten,[12] but of the same order of magnitude.

The fluctuations of the current of the elastically backscattered electrons have been measured, as a function of the temperature, for different states of the specimen surface characterized by the Auger spectra (Fig. 2). The example of the power spectral density functions (PSD) of the elastically backscattered electron current [for Pd(110) covered with sulfur and coadsorbed phosphorus] is presented in Fig. 3 for increasing sample temperatures. These functions do not show the character of analogous functions for field-emission current fluctuation or, e.g., STM tunneling current fluctuation.[4] Because of this fact, resulting from generally different physical mechanism of elastic backscattering, another interpretation of them is required. The power spectral density functions for low frequencies show distinct changes with increasing temperature in the range from 6 up to 10 Hz only. The increase of the fluctuation power in this range (i.e., of the integral of PSD over it) seems to be a good measure of the changes in PSD shape mentioned above. This quantity is obviously connected with a certain thermally activated process. So, it has been assumed to fulfill an Arrhenius-type relationship. For higher frequencies no clear and repeatable temperature dependence can be seen.

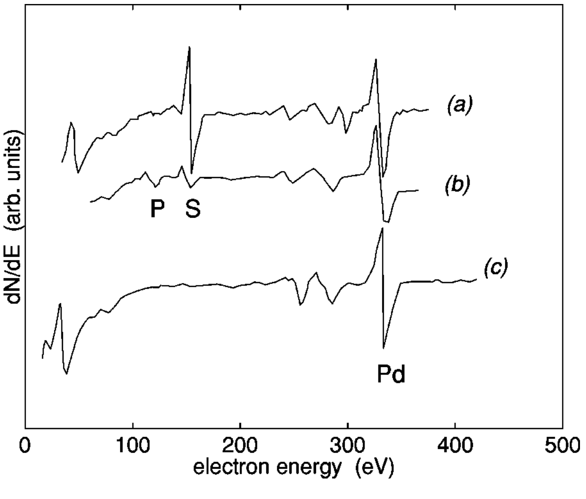

FIG. 2. Auger electron spectra measured for (a) palladium covered with sulfur, (b) palladium covered with sulfur and phosphorus, and (c) clean palladium.

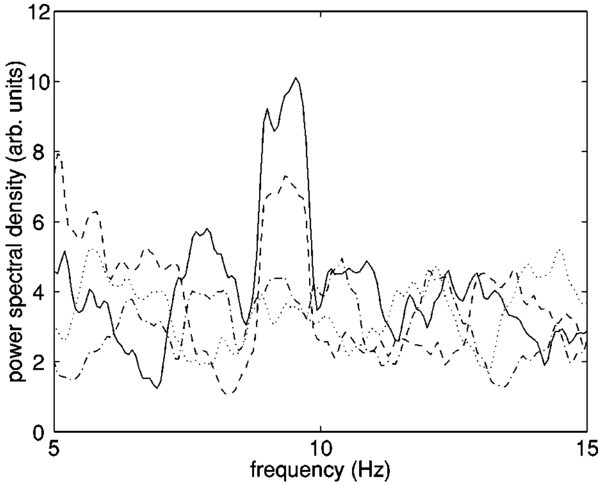

FIG. 3. Power spectral density of the current fluctuations of elastically backscattered electrons from Pd(110) surface; measured for sample temperatures: 514 K, solid line; 446 K, dashed line; 374 K, dash-dotted line; and 300 K, dotted line.

In Fig. 4 the results are presented for Pd(110) covered partly with sulfur (the Auger peak height ratio is $S_{152\ \mathrm{eV}}/\mathrm{Pd}_{327\ \mathrm{eV}} \gtrsim 1$), as can be seen in spectrum (a) of Fig. 2. The fluctuation power P in a frequency range of 6–10 Hz is plotted on a semilogarithmic scale versus reciprocal of the sample temperature T (Arrhenius plot). The experimental points can be quite well approximated (correlation coefficient $\rho \approx -0.80$) with a linear function $\ln(P) = \alpha 1/T + \beta$. Taking into account the relationship $-E_d/k_B = \alpha$ (where k_B is the Boltzmann constant) the activation energy of the pro-

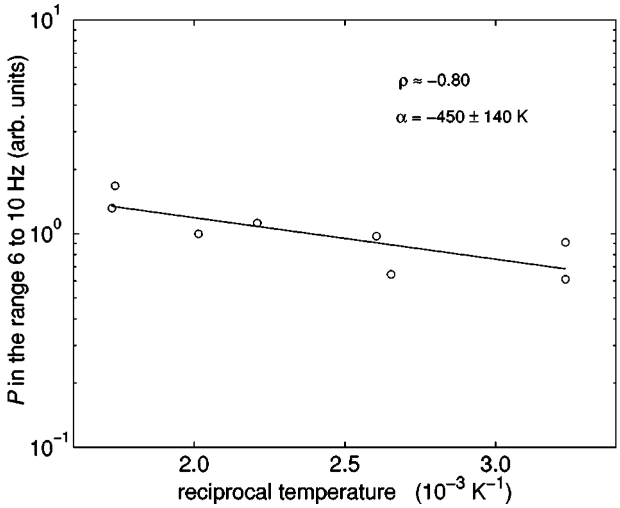

FIG. 4. Dependency of the current fluctuation power P of the electrons elastically backscattered from Pd(110) covered with sulphur on the reciprocal of the sample temperature (α is a slope of the regression line corresponding to $E_d = 39 \pm 12$ meV, and ρ is a correlation coefficient).

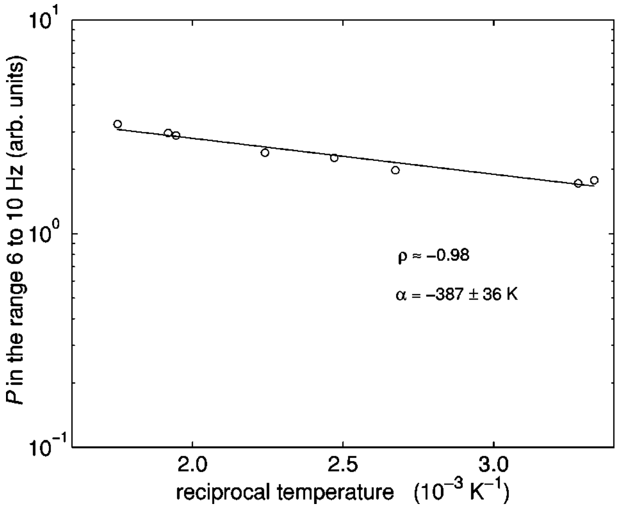

FIG. 5. Dependency of the current fluctuation power P of the electrons elastically backscattered from Pd(110) covered with sulphur and phosphorus on the reciprocal of the sample temperature (α is a slope of the regression line corresponding to $E_d = 33 \pm 3$ meV and ρ is a correlation coefficient).

cess E_d has been calculated. A value of α corresponds to the energy $E_d = 39 \pm 12$ meV. For palladium covered with sulfur and cosegregated phosphorus [spectrum (b) in Fig. 2], the results are presented in a way analogous to the previous case in Fig. 5. The linear approximation is even better (with $\rho \approx -0.98$), and a similar value of the activation energy equal 33 ± 3 meV has been calculated from the slope of the regression line. As we have not observed (by means of Auger electron spectroscopy) any significant changes of the total coverage of the surface in the temperature range from 300 up to 600 K (i.e., in the range in which measurements have been performed), we have assumed that the temperature-dependent fluctuations of the elastically backscattered electron current result from fluctuations of the local density of an adsorbate. The power of fluctuations of another origin (e.g., incident electron current fluctuation) is not expected to depend on the sample temperature, and has been treated as a background in our measurements. Taking this into account, the activation energy E can be interpreted as an activation energy for the surface diffusion of sulfur on palladium (110), or possibly of sulfur on sulfur. The two measured values of E_d do not differ from each other within the error limits; a value for the surface contaminated with phosphorus is, however, slightly lower. These values are about one order of magnitude smaller than known activation energies for a surface diffusion of sulfur on metals (nickel, tungsten).[12–14] On the other hand, they do not differ so much from the activation energy for diffusion of sulfur on sulfur (≈ 130 meV according to Ref. 15). Both measured values of E_d are also lower, but of the order of that found for sulfur on polycrystalline titanium.[5] It is worth mentioning that such low activation energies have recently been reported for diffusion of other adsorbates on palladium[16] or on related metals such as nickel.[17]

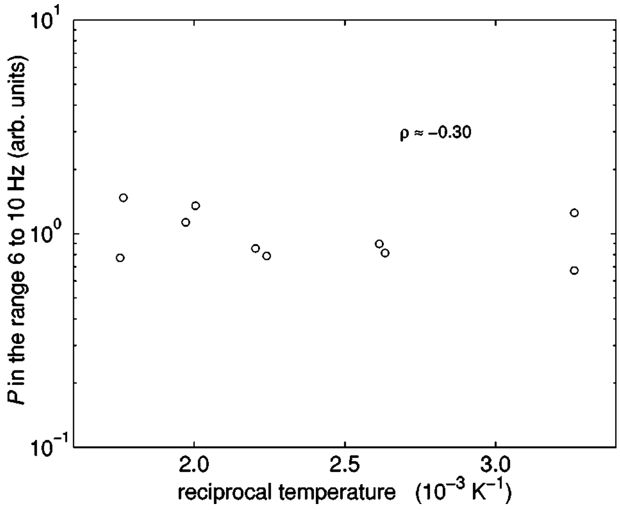

FIG. 6. Dependency of the current fluctuation power P of the electrons elastically backscattered from clean Pd(110) on the reciprocal of the sample temperature (ρ is a correlation coefficient).

For clean palladium [spectrum (c) in Fig. 2], no correlation between the sample temperature and the fluctuation power has been observed. The results for this case are presented for comparison in Fig. 6, in a way analogous to Figs. 4 and 5. The correlation coefficient $\rho \approx -0.30$ is very poor, and the relationship cannot be presented as a linear Arrhenius plot. The lack of a thermal dependency of the fluctuation power in the absence of an adsorbate confirms that such dependency is observed due to surface diffusion.

IV. CONCLUSIONS

A segregation of sulfur onto the Pd(110) surface takes place mainly at temperatures over about 700 K with the segregation energy equal to 310 ± 20 meV (per atom). On the surface covered with an adsorbate a dependence of fluctuation power on temperature for low frequencies can be observed. This relationship may be described by the Arrhenius law (i.e., $P \propto e^{-E_d/k_B T}$). The following values of activation energies (per atom) for surface diffusion have been obtained: 39 ± 12 meV for Pd(110) covered with sulfur, and 33 ± 3 meV for Pd(110) covered with sulfur and phosphorus. The low value of this energy matches the activation energy for sulfur on sulfur surface diffusion[15] rather than that for sulfur on metals. The diffusion activation energy does not depend significantly on the presence of phosphorus on the palladium surface. On the clean Pd(110) surface no dependence of fluctuation power on temperature has been observed.

ACKNOWLEDGMENT

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