O₂ ADSORPTION ON NON-UNIFORM FRACTAL SURFACES
OF COPPER FILMS

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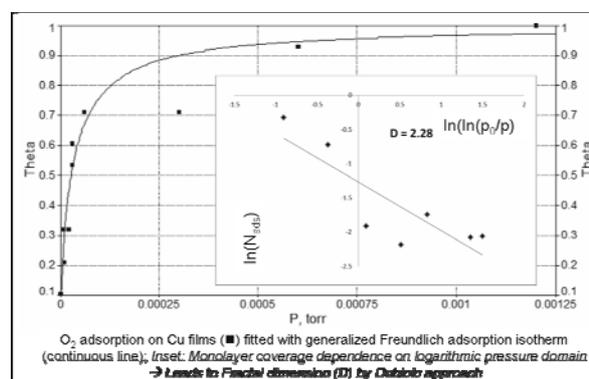"Ilie Murgulescu" Institute of Physical Chemistry of the Roumanian Academy, 202 Spl. Independentei, 060021 Bucharest, Roumania

Oxygen adsorption on copper thin films was investigated in a home-built high-vacuum setup equipped with turbomolecular and ionic pumps. Prior to each experiment (copper films deposition or oxygen admission), the pressure inside the working cell was about 5×10^{-8} Torr. Copper films were deposited by evaporation on polycrystalline W substrate. Oxygen adsorption on copper films was investigated at room temperature (300 K) at doses between 10 and 10^4 Langmuir (L).

Modeling of the adsorption data with Langmuir isotherm indicates the non-uniformity of the copper film surfaces. The isotherms corresponding to the exponential energy distribution (Boltzmann or Fermi-Dirac) of the adsorption centers match better the experimental data, from the point of view of correlation, standard errors, and attribution of the fitting parameters. The energetically non-uniform character of the adsorption sites could result from two processes: the thermal treatment of the as-deposited Cu films (biographic nonuniformity) and the rapid surface reconstruction, following the admission of the first oxygen doses (induced nonuniformity).

This is in line with fractal analysis performed by Dubinin approach, which emphasized that all analyzed surfaces exhibit fractal behavior from lower fractal dimensions (2.27-2.29), indicating smooth surfaces, to higher ones (2.70-2.80) corresponding to highly corrugated surfaces.

O₂ adsorption on Cu films (■) fitted with generalized Freundlich adsorption isotherm (continuous line); Inset: Monolayer coverage dependence on logarithmic pressure domain → Leads to Fractal dimension (D) by Dubinin approach

INTRODUCTION

Oxygen interaction with the copper surfaces, as with the other two (Au and Ag) metals from IB Group, is one of the major issues of catalysis. Metals from Group IB are used as catalysts such as Ag in the ethylene epoxidation reaction or as promoters and dopants for metallic and semiconductor catalysts (in the case of Cu and Au). Studies regarding the Cu / oxygen system have been conducted from low temperatures (30K)[1-3] to temperatures as high as 800 K.[4,5] In most of the cases it has been found that oxygen is adsorbed in a dissociated state or in an oxide configuration for $T \geq 300$ K. Molecular adsorption was observed at low temperatures, around 30 K,[1-3] in form of physical adsorption, or up to temperatures of 150 K, where weakly chemisorbed oxygen species were detected.[6-9]

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The formation of a strongly chemisorbed species, characteristic for the dissociative oxygen binding on the metallic surfaces, was identified at room temperature adsorption experiments based on UPS and ELS techniques.[10] In this case, the measurements of the variation of the Work Function (WF) revealed an increase of the WF, which corresponds to the negative charge of the oxygen atoms, in accordance with the results obtained in other oxygen / metal systems.[11-13]

In this paper, we have studied the adsorption of oxygen on copper films at room temperature. For this purpose, the copper films were evaporated on W substrate, and thermally treated up to 500 K. Further on, oxygen doses from 10 to 10^4 L were introduced in the working cell. The oxygen interaction with the copper films was studied by work function measurements, adsorption isotherms and fractal analysis.

RESULTS AND DISCUSSION

1. Copper films deposition

The thickness of the deposited film (copper) was followed by monitoring the current-voltage (I/V) curves, as it was used a diode-like configuration of the experimental cell. As soon as there is no displacement of the I/V curve, it is considered that the deposited metal layer has the bulk characteristics of the deposited metal.[14] The as-deposited Cu films were further thermally treated up to 500 K in order to obtain a reproducible surface (from WF variation point of view).

It is known from the literature that tungsten (the material from which the substrate was made) exhibits a work function (WF) value of 4.5 eV, while for the polycrystalline Cu the following values are reported: 4.55, 4.46 and 4.61 eV. In our experiments, the formation of the Cu layer was achieved with both low and high deposition rates, each time obtaining similar curves for the variation of the WF with the thickness of the deposited layer (**Fig. 1**). The calculated dipole moment for the adsorbed layers is the maximum for the first layer, corresponding to the ascending portion of the WF curve, then decreases and reaches constant values at 3-4 adsorbed layers when the extraction work is equal to that of the deposited film (Cu) adsorbed (end of the WF variation curve).[15]

Depending on the deposition rate, the WF was found to vary in our experiments from 0.16 eV to 0.445 eV for the Cu films evaporated on W substrate.

2. Oxygen adsorption on Cu films

Following the thermal treatment of the polycrystalline copper film, required to obtain a reproducible (standard) surface, the introduction of increasing molecular oxygen doses and the measurement of the WF variations caused by the adsorption were studied. The working pressure in the cell was about 5×10^{-8} Torr. After each oxygen dose, the enclosure was pumped, returning to normal working pressure of about 5×10^{-8} Torr. Generally, simple gases (as in the case of oxygen) act as electron acceptors, producing ionic-like covalent adsorption, which results in the formation of a double layer of negative pole outside. This leads to an increase in the WF of the metal (Cu) on which the adsorption has taken place. Indeed, we observed this behavior (positive displacements of the current / voltage characteristics) in the study of copper oxygen adsorption (**Fig. 2**). The maximum variation of the WF variation obtained in this experiment was 0.65 eV for a total oxygen dose of 23000 L.

From different measurements, we obtained different values of the WF variation during oxygen adsorption on copper films (exemplified in **Table 1**). The differences obtained in the WF variation for two types of Cu deposition rates could be explained by the fact that in the case of the low deposition rates, both in the volume of the deposited film and on its surface as well, different gaseous products could be adsorbed from the residual atmosphere (the gas composition inside the working cell during experiments).

3. Nonuniform character of the adsorption isotherms

Further on, the adsorbed oxygen doses were expressed as adsorption isotherms, by calculating the oxygen coverage in function of its pressure. In **Fig. 3** we present the adsorption isotherm obtained during oxygen adsorption on a Cu layer deposited at a low rate and thermally treated at about 450 K for 30 minutes.

The oxygen adsorption isotherm was fitted with various two-parameter and one-parameter isotherm equations (**Fig. 3**), obtained for various site-distributions under the energetically non-uniform surface model assumptions.[16-18]
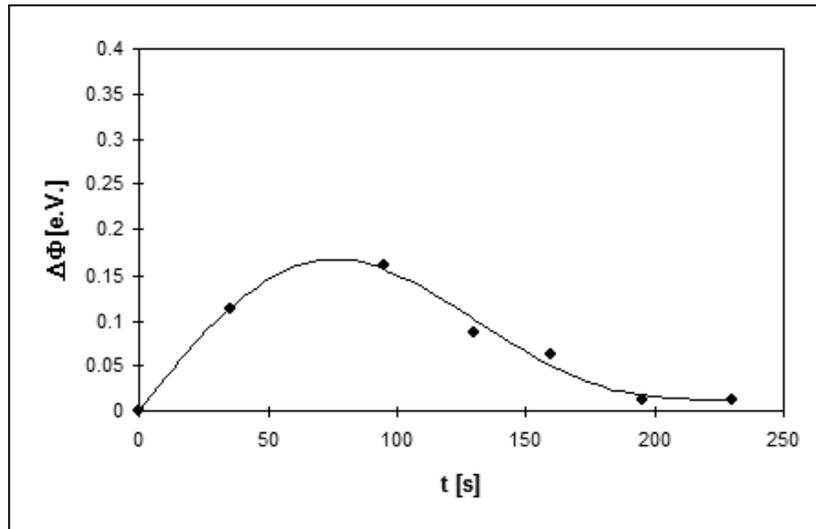
Fig. 1 – Typical WF variation ($\Delta\Phi$) for Cu films deposition on polycrystalline W substrate.
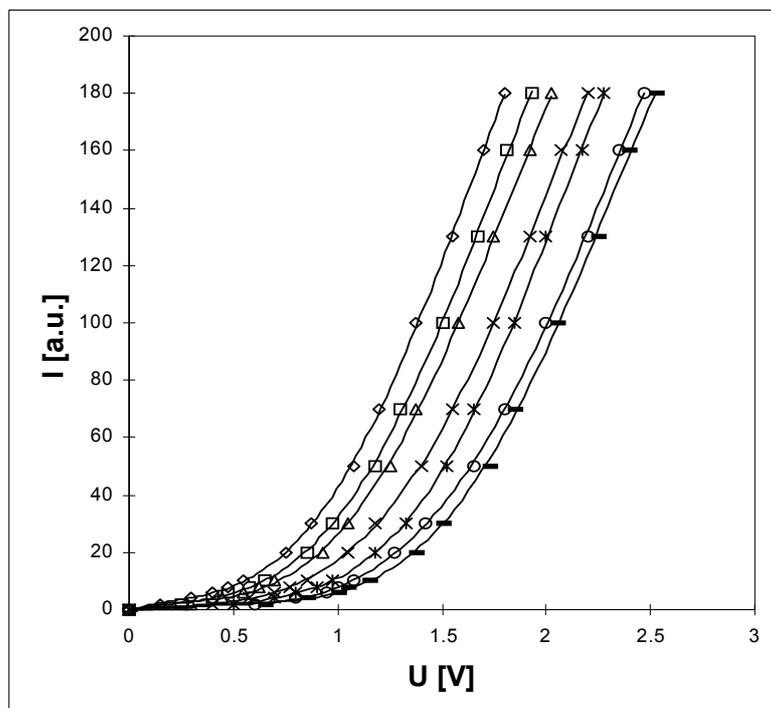

Fig. 2 – Displacement of current (I) / voltage (V) curves during oxygen adsorption on copper.

Table 1

WF variation ($\Delta\Phi$) function of the adsorbed oxygen doses

Cu film (Experiment N^o)	Deposition rate	$\Delta\Phi_{max}$ (eV)	Oxygen Doses (L)
1	Low	0.70	22560
2	Low	0.52	46440
3	Low	0.15	23505
4	Low	0.66	47910
5	Low	0.29	4170
		0.48	29505
		0.72	41505
		0.63	53505
6	High	0.32	76445
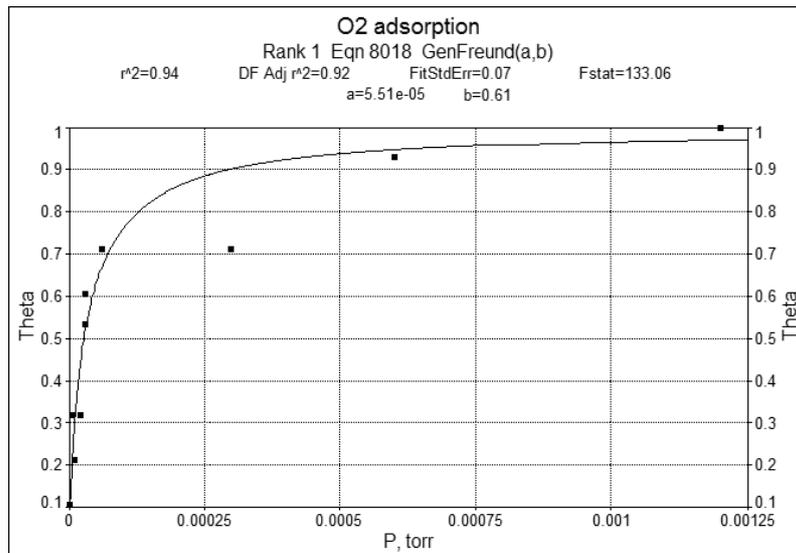
Fig. 3 (a)

r² Coef Det	DF Adj r²	Fit Std Err	F-value
0.94	0.92	0.07	133.06

Parm	Value	Std Error	t-value	95% Confidence Limits		P>|t|
a	*5.51e-05*	*3.70e-05*	*1.48*	*-3.02e-05*	*14.05 e-05*	*0.17*
b	*0.61*	*0.22*	*2.72*	*0.09*	*1.13*	*0.02*
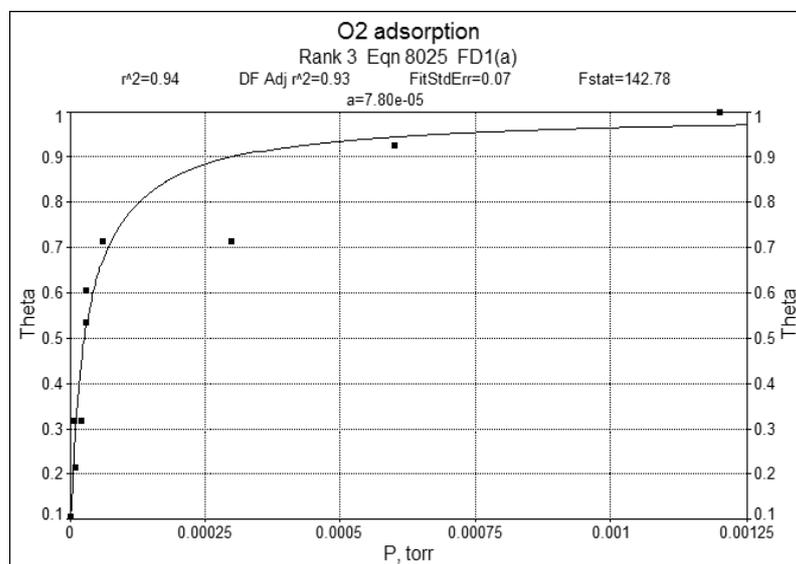
Fig. 3 (b)

r² Coef Det	DF Adj r²	Fit Std Err	F-value
0.94	0.93	0.07	142.78

Parm	Value	Std Error	t-value	95% Confidence Limits		P>|t|
a	7.80e-05	1.22e-05	6.39	5.04e-05	10.56 e-05	13 e-05
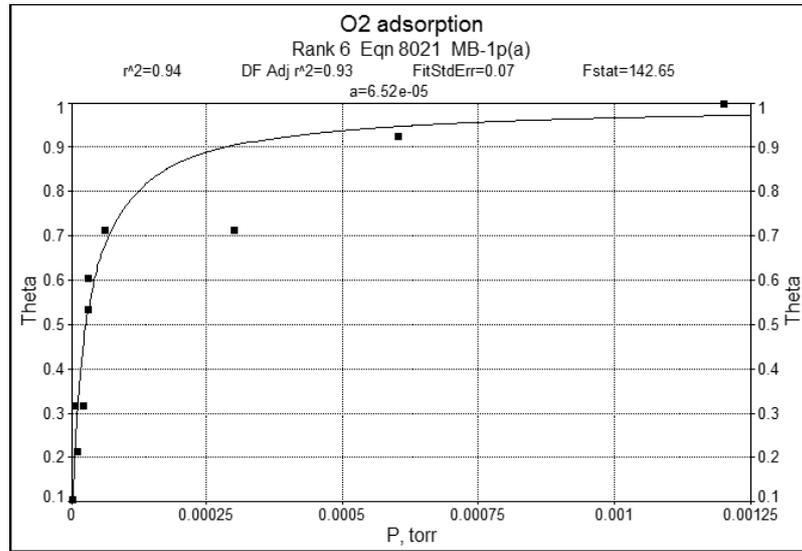
Fig. 3 (c)

r² Coef Det	DF Adj r²	Fit Std Err	F-value
0.94	0.93	0.07	142.65

Parm	Value	Std Error	t-value	95% Confidence Limits		P>|t|
a	6.52e-05	9.97e-06	6.54	4.26e-05	8.78e-05	11e-05
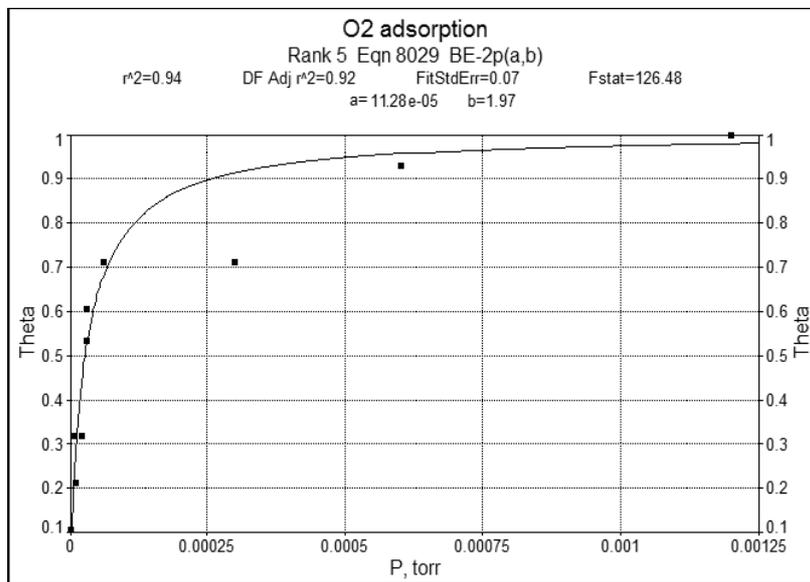
Fig. 3 (d)

r² Coef Det	DF Adj r²	Fit Std Err	F-value
0.94	0.92	0.07	126.48

Parm	Value	Std Error	t-value	95% Confidence Limits		P>|t|
a	11.28 e-05	2.14e-05	5.25	6.32e-05	16.23e-05	77e-05
b	1.97	0.08	23.89	1.78	2.16	0.00
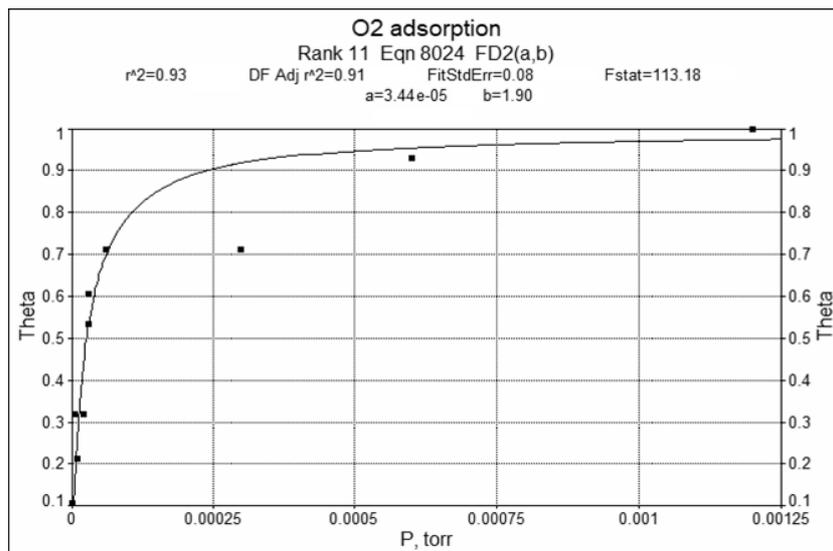
Fig. 3 (e)

r² Coef Det	DF Adj r²	Fit Std Err	F-value
0.938	0.91	0.08	113.18

Parm	Value	Std Error	t-value	95% Confidence Limits		P>|t|
a	3.44e-05	7.76e-06	4.44	1.65e-05	5.24e-05	216e-05
b	1.90	0.09	20.36	1.68	2.11	0.00

Fig. 3 – Adsorption isotherms obtained for the oxygen / copper system, fitted with the isotherm equations derived according to differently distributed adsorption sites: (a) - Sips exponential (generalized Freundlich isotherm); (b) - Fermi-Dirac (1 parameter); (c) – Maxwell – Boltzmann (1 parameter); (d) Bose-Einstein (2 parameters); (e) – Fermi-Dirac (2 parameters). Fit characteristics are given below each figure (below Fig. 3a, the uncertainties in the estimation of the fitting parameters are italicized).

The distribution functions corresponding to the best fits presented in **Fig. 3 (b-e)** are plotted in **Fig. 4** against the adimensional adsorption energy, q/RT.

There are several features in Figs. 3 and 4 that deserve a special attention:

(i) There is an inherent scatter of the experimental data. For this reason, the Lorentzian robust fitting was utilized in TableCurve v. 5.01 fits presented in Figs. 3. All isotherm equations were "user-defined" in TableCurve options.

(ii) The so-called "Generalized Freundlich isotherm" (GF), derived by Sips[16] in terms of the Stieltjes transform solution of the adsorption integral equation, seems the best fitting function in terms of the statistical R^2 and F_{stat} parameters. However, as evidenced in **Fig. 3a**, uncertainties in the estimation of the fitting parameters (italicized values) prevent the use of this function for the present data.

(iii) In general, one-parameter functions (overall isotherm equations) are better in terms of the parameter uncertainty: **Figs. 3(b) and 3(c)** corresponding to isotherm equations obtained for Fermi-Dirac (FD) and Maxwell-Boltzmann (MB)

site-distributions, respectively. Such distributions predict a considerable number of sites with adsorption energy close to zero, which are physically unrealistic.

(iv) A solution to the above problem is offered by truncation of the distribution to some lower limit of the adsorption energy that becomes a second fitting parameter in the corresponding isotherm equation, the value of which is obtained in the fitting process. For the MB distribution this equation gives a much worse fit (in terms of parameter errors) than GF, so that it is not presented in **Figs. 3**.

(v) There are two "truncated" distributions that give similar results in terms of goodness of fit: the Bose-Einstein (which is naturally truncated because of normalization requirements) - leading to "BE-2" isotherm, and the Fermi-Dirac one – leading to the "FD-2p" isotherm. Both these equations correspond to similar distributions, as presented in **Fig. 4**. Discriminating between the two is the most difficult within most adsorption data available, a phenomenon long-ago acknowledged by Sips.[16]
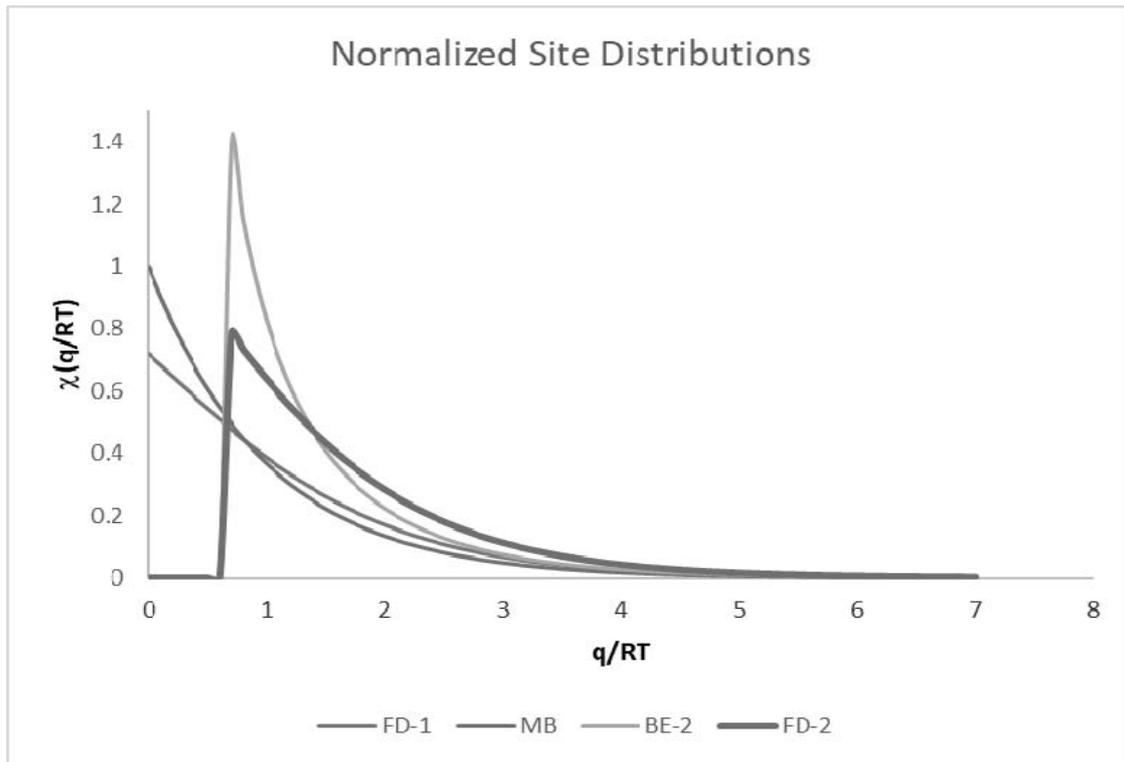
Fig. 4 – Site distributions corresponding to various isotherm equations utilized for modeling the experimental isotherm given in Fig. 3. FD = Fermi-Dirac, BE = Bose-Einstein, MB = Maxwell-Boltzmann.

4. Fractal analysis of oxygen adsorption isotherms

In nature, surfaces usually exhibit fractal behavior, instead of Euclidian geometric properties. This means that geometric irregularities and defects, even at molecular scale are self-similar[19]. Fractal dimensions describing such surfaces take values in the whole range ($2 \div 3$), where D=2 (or close to 2) indicates smoothness and D close to 3 indicates a highly irregular surface.

The surface fractal dimension can be computed by fitting a single adsorption isotherm with the appropriate fractal isotherm.

In the following we shall use the Dubinin approach[20] for adsorption on heterogeneous microporous solids to compute the fractal dimension of the Cu films. The Dubinin approach was developed by Avnir and Jaroniec[21] considering a fractal distribution of surface micropores. They showed that for microporous solids in the region of $p/p_0 = 0.05$ to the micropore filling pressures, the Dubinin isotherm can be analytically integrated, leading to the following equation:

$$\theta = \frac{1}{2} C r \left(\frac{3-D}{2} \right) m^{-(D-3)/2} A^{-(3-D)} \quad (1)$$

where Γ is the gamma function, C and m are constants, D is the fractal dimension, and A = RT $\ln(p_0/p)$ is the adsorption potential.

Equation (1) can be written in a practical way, as:

$$\theta = K \left[\ln \left(\frac{p_0}{p} \right) \right]^{-(3-D)} \quad (2)$$

At low p/p_0 values, the monolayer coverage highly depends on fractal dimension, so the form depicted in Eq. (2) can be used to compute fractal dimension by fitting experimental data (**Table 2**).

All analyzed surfaces exhibit fractal behavior: the surfaces described in experiments "3" and "4" have lower fractal dimensions, 2.27-2.29, indicating smooth surfaces; meanwhile the others are highly corrugated surfaces, with fractal dimensions between 2.70-2.80. The monolayer coverage dependence on logarithmic coverage, used to compute fractal dimension by fitting experimental data, is shown in **Fig. 5** for experiments denoted as 1, 2, 3 and 5 (described in **Table 1**).

The sample from experiment "5" (on which the adsorption experiment was performed step-by-step – see **Table 1**) exhibits two fractal dimensions: one

of them, the lower one (1.87) characteristic to the lower equilibrium pressures, corresponds to the distribution of the adsorption centers, at weak micropore filling, meanwhile the higher fractal dimension has a pure geometrical meaning, the surface self-similarity. The same behavior exhibits the sample from experiment "1", with a very low fractal dimension characterizing the distribution of adsorption centers (0.86).
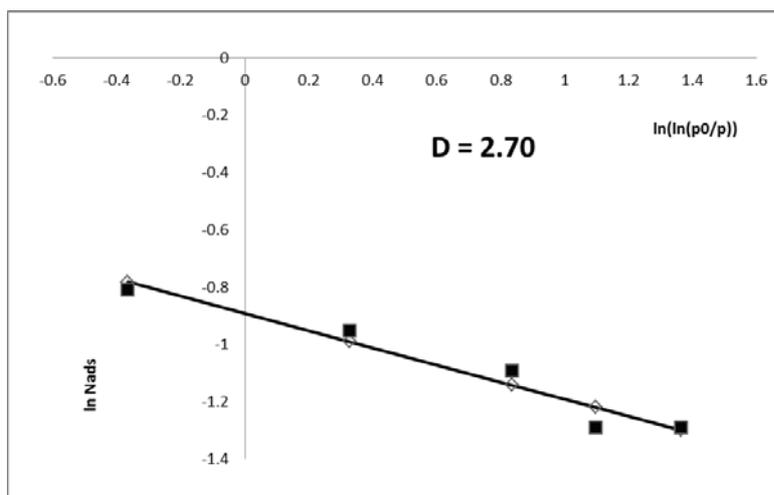
Table 2

Fractal dimensions obtained using direct fitting of experimental data based on fractal adsorption isotherm from eq. (2)
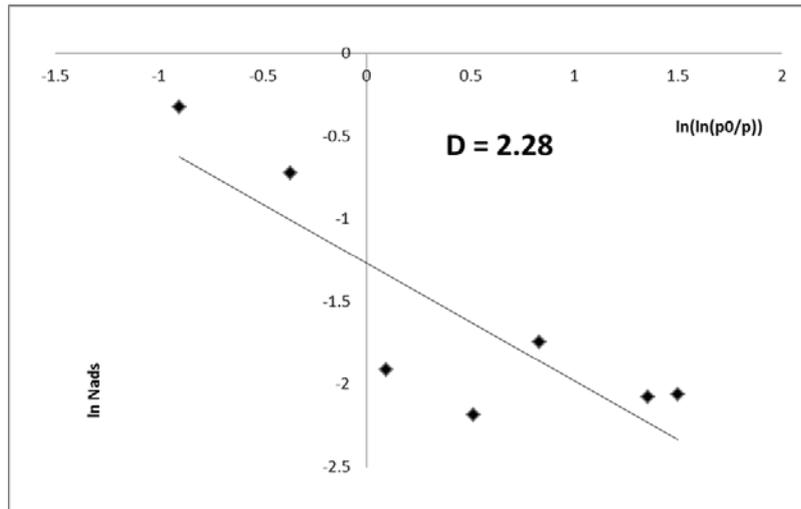
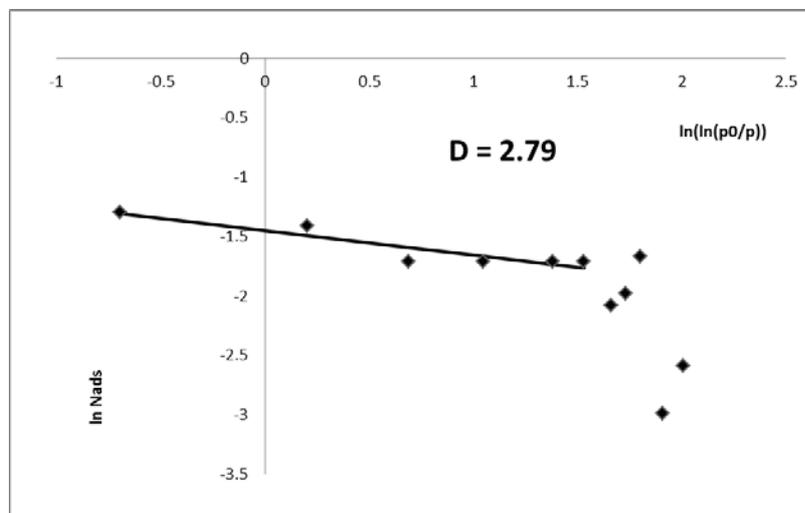| Cu film (Experiment N^o)	p/p_0 domain	Fractal dimension (D)
1	$0.05 \geq p/p_0 \geq 0.83e\text{-}03$	0.86 ± 0.38
	$p/p_0 \geq 0.05$	2.82 ± 0.11
2	$p/p_0 \geq 0.01$	2.70 ± 0.04
3	$p/p_0 \geq 0.01$	2.29 ± 0.20
4	$p/p_0 \geq 3e\text{-}03$	2.27 ± 0.10
5	$0.05 \geq p/p_0 \geq 1.25e\text{-}03$	1.87 ± 0.09
	$p/p_0 \geq 0.05$	2.71 ± 0.09
6	$p/p_0 \geq 9e\text{-}03$	2.79 ± 0.04
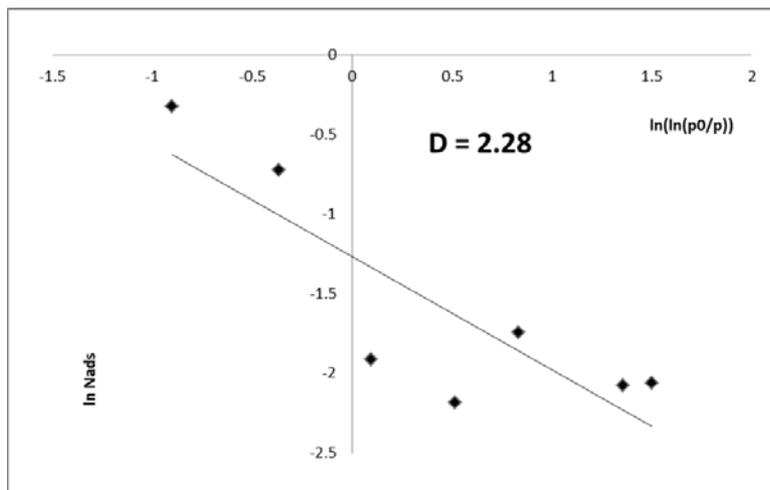
(a) Exp 1

(b) Exp 2

(c) Exp3

(d) Exp5

Fig. 5 – Monolayer coverage dependence on logarithmic pressure domain, used to compute fractal dimension
by fitting the experimental data based on Dubinin approach.

EXPERIMENTAL

Surface studies require ultra-high vacuum conditions.[4] Therefore all the experiments described here were performed in a high vacuum home-made setup, including turbomolecular and ionic pumps, so that the base pressure before each experiment was 5×10^{-8} Torr.

The anode current measurement (diode-configuration cell) was performed with a Tesla type BM 483 picoamperometer. The electrical signal was recorded on the Y axis of a HP 7000 AM Hewlett Packard plotter function of the applied voltage.

CONCLUSIONS

The results obtained in the study of copper oxygen adsorption deposited on polycrystalline tungsten revealed the following aspects: (i) The variation of the WF following deposition of copper on polycrystalline tungsten led to a $\Delta \Phi$ vs. thickness dependence in good agreement with literature data; (ii) the adsorption of (molecular) oxygen at room temperature on thin copper layers leads to the formation of a superficial structure characterized by a positive variation of the WF variation (charge transfer from the substrate to the adsorbate); (iii) Fitting the adsorption data with various isotherm equations indicates the non-uniform character of the deposited copper film surfaces (corresponding to an "exponential-type" distribution of the adsorption sites energies); (iv) All analyzed surfaces exhibit fractal behavior: while lower values, characteristic to the lower equilibrium pressures, corresponds to the distribution of the adsorption centers at weak micropore filling, higher fractal dimensions have pure geometrical meaning in terms of surface self-similarity.

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