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Characterization of the Cu(110)-(2×1)O reconstruction by means of molecular adsorption

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The binding energies and the structural properties of atoms and molecules adsorbed on the Cu(110)-(2×1)O surface are intimately related to the precise geometry of the surface reconstruction. In particular, the adsorbate-substrate interaction strongly depends on the characteristic parameters of the surface reconstruction, namely, the relaxation between the first two Cu planes, the oxygen position above the surface, and the ionic nature of the Cu-O bond. We propose a reliable estimate of these parameters by comparing semiempirical interaction potential calculations to recent experimental results on the adsorption properties of Xe and N_2 monolayers on Cu(110)-(2×1)O. [S0163-1829(98)07639-5]

I. INTRODUCTION

The chemisorption of H, O, or S is known to induce a reconstruction of the more open surfaces of various metals such as Cu or Ni.[1] These reconstructed surfaces also constitute a class of substrates for the physisorption of atomic or molecular species. Comparing the adsorption properties and the adlayer structure with those of the corresponding *unreconstructed* substrates, one may expect to learn about the influence of the surface geometry and electronic structure on the details of physisorption process.

In this aim, we have studied the adsorption of Xe and N_2 on the clean Cu(110) surface[2–5] and on the oxygen-reconstructed Cu(110)-(2×1)O surface.[6,7] The adsorption energies and the phase diagrams have been determined using helium-atom scattering and thermal-desorption spectroscopy. As a result, it has been shown that the two surfaces behave very differently with respect to the physisorption of Xe and N_2. Any quantitative analysis of these results primarily relies on the accuracy of the substrate geometry and of the potential parameters used to describe the adsorbate-substrate interactions. Whereas the interaction of Xe and N_2 with the unreconstructed (bulk) substrate was previously derived from experiments on the bare Cu(110) surface[2,5] the parameters connected to the oxygen-induced reconstruction had to be extracted from the literature. In this context, it was realized that the adsorbate geometries and binding energies crucially depend on the position d_O and ionic character q_O of the oxygen atoms, and on the interlayer spacing d_{12} between the first two Cu planes of the Cu-O surface. The correct choice of these values is, therefore, of great importance. Conversely, we may take advantage of the high sensitivity of the adsorbate geometry and the binding energies on the details of the surface reconstruction to determine reliable values for the parameters q_O, d_O, and d_{12} from the comparison with the experimental data, and, in this way, to extract accurate information on the structure of the reconstructed surface.

In this paper we discuss how to use the physisorption of simple molecules as a sensitive probe of the surface geometry and charge distribution. This approach is based on the assumption that the physisorption does not significantly affect the surface reconstruction nor the strong ionic or metallic Cu-O and Cu-Cu bonds, respectively. This assumption is consistent with the observation, using helium-atom scattering, of the structure of the Xe (or N_2) recovered (2×1) Cu-O phase which exhibits the same diffraction peaks as those of the bare Cu-O surface. Moreover, it can be argued that simple physisorbates are probably a very adequate and softer probe of the substrate reconstruction when compared to more perturbative techniques based on electrons and x-ray beams, and to chemisorbed species.

In Sec. II, we present the available experimental data on the oxygen-induced surface reconstruction of the Cu(110) surface, and discuss the values of the relevant parameters characterizing the surface geometry. In Sec. III, we describe calculations predicting the stable monolayer phases for Xe and N_2 on the Cu(110)-(2×1)O surface, and the corresponding adsorption energies. In Sec. IV, these results are compared to the experimental data. From this comparison we extract a well-defined set of values for q_O, d_O, and d_{12} which can consistently explain both the physisorption of Xe and N_2 on the reconstructed Cu(110)-(2×1)O surface.

II. GEOMETRY OF THE CU(110)-(2×1)O SURFACE

There has been a long debate on the nature of the oxygen-induced surface reconstruction of the Cu(110) surface. Since the pioneering work of Ertl[8] it has been well known that the adsorption of half a monolayer of oxygen results in a 2×1 superstructure. Low-energy ion-scattering experiments[9–12] reported a missing-row reconstruction where every other [001] Cu row on the surface is absent. This model was also supported by surface extended x-ray-absorption fine-structure measurements.[13,14] On the other hand, high-energy ion-scattering[15] and scanning tunneling microscopy (STM) (Ref. 16) suggested a buckled-row model in which every second row is not missing but shifted outwards.[17] This was contradicted by x-ray diffraction measurements,[15] low-energy electron diffraction,[18] and impact collision ion scattering spectroscopy (ICISS),[19,20] again confirming the

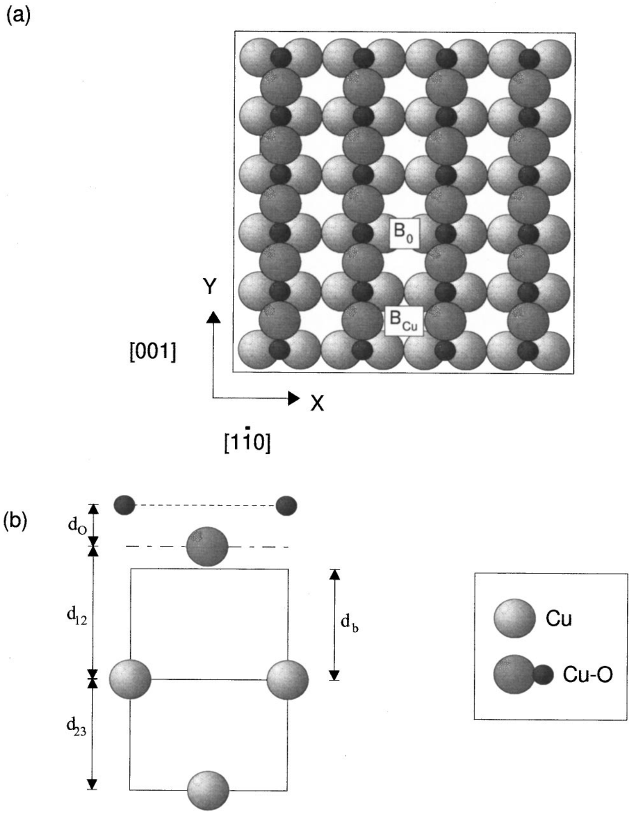

FIG. 1. (a) Top view of the reconstructed Cu(110)–(2×1)O surface (added row model). The oxygen and copper bridge sites are labeled B_{O} and B_{Cu}. (b) Side view of the Cu(110)–(2×1)O substrate. The large and small circles correspond to copper and oxygen atoms, respectively. $d_{pp'}$ denotes the interlayer spacing between Cu planes p and p'. In our case $d_{23}=d_b$, the separation of (110) planes in the bulk Cu.

missing-row-type reconstruction. More recent STM data[21,22] could finally settle the discussion in favor of a missing-row-type reconstruction which, however, should be viewed as an ''added-row'' phase due to the mechanism of its formation. In fact, the restructuring proceeds via the nucleation of added Cu-O rows running along the [001] direction which aggregate into striped islands[23] with a 2×1 structure, eventually leading to a homogeneous Cu(110)-(2×1)O phase for an oxygen coverage of 0.5. The added-row mechanism was also confirmed in ICISS experiments,[24] and now seems to be generally admitted. Furthermore, all studies seem to agree that the oxygen is located in the long bridge site between neighboring Cu atoms along the added rows, but they disagree on the height of the oxygen atom above or below the first copper layer, and on the extent of the interlayer relaxation between the topmost Cu layers. Calculations based on the effective medium theory,[25] a semiempirical tight-binding approach,[26] the local-density approximation,[27] and an *ab initio* molecular-orbital cluster model[28] were performed to study the surface relaxation and the oxygen position.

A summary of the structural parameters pertaining to the reconstruction (see Fig. 1) was presented in Refs. 20 and 27. It shows that the lateral displacements (parallel to the surface) of the Cu atoms remain very small, as does the relaxation between the second and third Cu planes. In contrast, the spacing d_{12} between the first two Cu planes and the

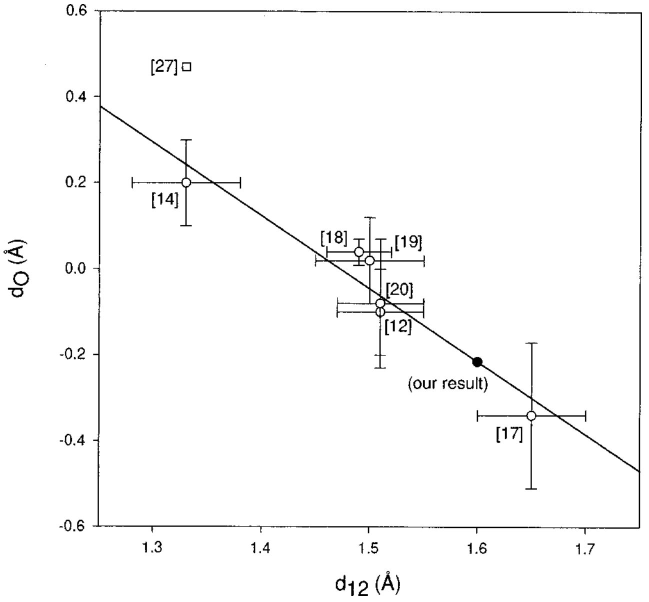

FIG. 2. Experimental values of the interlayer spacing d_{12} between the first two Cu planes and of the position d_{O} of the oxygen with respect to the topmost Cu plane (open circles). The linear regression through the data points (solid line) shows the strong correlation between the two parameters [cf. Eq. (1)]. The filled circle indicates our best-fit parameter set $d_{12}=1.60\pm0.05$ Å and $d_{\mathrm{O}}=-0.21\pm0.1$ Å. The open square represents the calculation of Ref. 27. The error bars are given for each bit of experimental data.

height d_{O} of the oxygen atoms above the Cu added rows exhibit a significant variation, depending on the data source. An examination of these data reveals that the values for d_{O} and d_{12} are strongly correlated (Fig. 2), and that the overall trend can be accounted for by a simple linear regression:

$$d_{\mathrm{O}}=-1.695\times d_{12}+2.497\ \text{Å}. \tag{1}$$

The coefficients have no physical meaning, but this correlation can nevertheless be used to limit the discussion to only two independent parameters d_{12} and q_{O}. Information on the charge transfer q_{O} from Cu to the oxygen atoms is not available from experiments, and the single known value is the one provided by the *ab initio* calculation in Ref. 28, indicating a charge transfer of about $-(1.05\pm0.02)e$ (e is the electronic charge). This is quite a large value and, therefore, we consider q_{O} as an adjustable parameter.

III. THEORETICAL MODEL AND RESULTS

The interaction between a single N_2 molecule and the Cu-O substrate is described as a sum of (i) the Lennard-Jones potential V_{LJ} which accounts for the dispersion-repulsion contribution, (ii) the induction potential V_I which characterizes the polarization of the N_2 electronic cloud by the electric field due to the surface charges on the oxygen and copper atoms, and (iii) the electrostatic potential V_E between the quadrupole moment of N_2 and the surface charges.[7] The interaction between Xe and the Cu-O surface contains only the first two potential terms.[6] This adsorbate-substrate interaction potential is written in the two-dimensional (2D) reciprocal space defined by the 2×1 unit cell with area $S=2\sqrt{2}a^2$

TABLE I. Lennard-Jones potential parameters for the N_2-CuO and Xe-CuO interactions.

	C_6 (eV Å^6)	C_{12} (eV Å^{12})
N-N	16.8	22 524.0
N-Cu	36.5	102 035.6
N-O	16.4	17 953.6
Xe-Xe	342.0	1 176 056.0
Xe-Cu	159.0	687 015.1
Xe-O	108.9	171 162.9

($a=2.55$ Å is the lattice parameter) of the Cu-O substrate. Let $\mathbf{g}=g_x(2\pi/a)\mathbf{x}+g_y(\sqrt{2}\pi/a)\mathbf{y}$ be the 2D reciprocal vector (with g_x and g_y integer numbers) and $\mathbf{R}_{isp}=\mathbf{r}_{i\parallel}-\tau_{sp}+z_{isp}\mathbf{z}$ be the relative distance between the ith adsorbate atom at the position $\mathbf{R}_i(\mathbf{r}_{i\parallel},z_i)$ and the sth oxygen or copper atom in the pth plane of the substrate, where τ_{sp} defines the lateral position of the sth atom of the pth plane in the unit cell [Fig. 1(a)]. The potential Φ_S at the point $\mathbf{R}_i$ which is due to the surface charges q_s on the oxygen and copper atoms of the reconstructed substrate plane is expressed as

$$\Phi_S(\mathbf{R}_i)=\frac{2\pi}{S}\sum_{s,p}\sum_{\mathbf{g}}\frac{q_s}{g}e^{i\mathbf{g}(\mathbf{r}_{i\parallel}-\tau_{sp})}e^{-gz_{isp}}. \tag{2}$$

V_{LJ} is then given by

$$V_{\mathrm{LJ}}=\frac{2\pi}{S}\sum_i\sum_{s,p}\sum_{\alpha=6,12}\frac{(-1)^{\alpha/2}C_\alpha^{is}}{\left(\dfrac{\alpha}{2}-1\right)!}\sum_{\mathbf{g}}e^{i\mathbf{g}(\mathbf{r}_{i\parallel}-\tau_{sp})}\times\left(\frac{g}{2z_{isp}}\right)^{(\alpha/2)-1}K_{(\alpha/2)-1}(gz_{isp}) \tag{3}$$

where C_α^{is} characterizes the potential parameters ($\alpha=6$ and 12) for the (i,s) atomic pair (Table I), and $K_{(\alpha/2)-1}$ is the modified Bessel function of integer order.

V_I can be expressed as

$$V_I=-\tfrac{1}{2}\sum_i\nabla\Phi_S(\mathbf{R}_i)\alpha_i\nabla\Phi_S(\mathbf{R}_i), \tag{4}$$

where α is the dipolar polarizability tensor for the Xe or N_2 molecules which takes the value $\alpha_{\mathrm{Xe}}=4.0$ Å^3 and $\alpha_{N_2}=1.76$ Å^3 in the molecular frame. Finally, V_E (for N_2 only) is given by

$$V_E=\sum_i q_i\Phi_S(\mathbf{R}_i), \tag{5}$$

where q_i are charges distributed on the N_2 molecule to describe its quadrupolar nature ($q_i=-0.405e$ on each N site, and $0.810e$ at the molecule center of mass).

V_{LJ} in Eq. (3) depends on the reconstruction parameters d_{O} and d_{12} through z_{isp}, whereas the two other potentials [Eqs. (4) and (5)] also depend on q_{O} through the charge q_s entering Φ_S in Eq. (2). The lateral interactions (between Xe atoms or between N_2 molecules) are described by the usual dispersion-repulsion and electrostatic (for N_2, only) potentials.[2–5] The values of the potential parameters are given in Table I.

The total potential, including the adsorbate-substrate interactions and the lateral adsorbate interactions, is minimized with respect to the position of the centers of mass of the adsorbed molecules and to the orientation of the molecular axes (for N_2), treating d_{12} and q_{O} as parameters. The numerical method is similar to previous studies,[2–7] except that, here, the values of d_{12}, q_{O}, and d_{O} [through Eq. (1)] are varied.

A single Xe atom is adsorbed inside the troughs between neighboring Cu-O added rows. The energetically favored site corresponds to an oxygen-bridge site B_{O} for small values of d_{12}, but changes to a copper-bridge site B_{Cu} for large values of d_{12} [Fig. 1(a)]. With increasing Xe coverage, the competition between the lateral Xe-Xe interactions and the substrate corrugation, which is directly related to the value of d_{O} and, hence, to d_{12}, tends to favor commensurate Xe structures for $d_{12}<1.30$ Å and for $d_{12}>1.70$ Å. In contrast, within the range $1.30\ \text{Å}\leqslant d_{12}\leqslant 1.70$ Å, the stable Xe phase becomes incommensurate, as observed in the experiment.[6] The calculated adsorption energy depends almost linearly on d_{12} within this range of values but it is nearly independent of the charge q_{O} [Fig. 3(a)]. The experimental value of 223 ± 6 meV is obtained in the calculations for $d_{12}=1.60$ Å, with an uncertainty which further confines the values for d_{12} to

$$1.55\ \text{Å}\leqslant d_{12}\leqslant 1.65\ \text{Å}. \tag{6}$$

In the case of N_2, we proceed in the same way. Three different adsorption sites for a single adsorbed molecule are obtained in the calculation, depending on the value of d_{12}. For $d_{12}<1.30$ Å, the molecule is located inside the [001] troughs above a Cu bridge B_{Cu} with its axis normal to the surface. For $d_{12}>1.67$ Å, the molecule lies flat above an oxygen-bridge site B_{O} with its axis perpendicular to the Cu-O rows. For $1.30\ \text{Å}\leqslant d_{12}\leqslant 1.67$ Å, the molecule is also lying flat, but with its axis parallel to the rows. At higher coverage, the N_2 molecules form a 2D lattice gas if d_{12} is inside the range $1.30\ \text{Å}\leqslant d_{12}\leqslant 1.67$ Å, while an ordered 2×1 commensurate structure is obtained outside this range. The lattice-gas formation is in agreement with the He scattering data, indicating a low-density structure in this coverage regime.[7] The adsorption energy for N_2 on the reconstructed surface depends strongly on the values of both d_{12} and q_{O}, the latter dependence being specific to N_2 [Fig. 3(b)] when compared to Xe [Fig. 3(a)]. In Fig. 3(b) we indicated the experimental value of the adsorption energy (125 ± 6 meV) for comparison with the calculated energy curves for N_2. We find that the distance d_{12} which gives the correct experimental value increases from 1.49 to 1.63 Å when the charge transfer increases from $0.5e$ to $1.0e$. Taking into account the experimental error bars, we obtain the following ranges for d_{12}, depending on q_{O}:

$$\begin{aligned} &1.30\ \text{Å}\leqslant d_{12}\leqslant 1.58\ \text{Å} \quad \text{for } q_{\mathrm{O}}=-0.5e,\\ &1.51\ \text{Å}\leqslant d_{12}\leqslant 1.65\ \text{Å} \quad \text{for } q_{\mathrm{O}}=-0.8e,\\ &1.57\ \text{Å}\leqslant d_{12}\leqslant 1.70\ \text{Å} \quad \text{for } q_{\mathrm{O}}=-1.0e. \end{aligned} \tag{7}$$

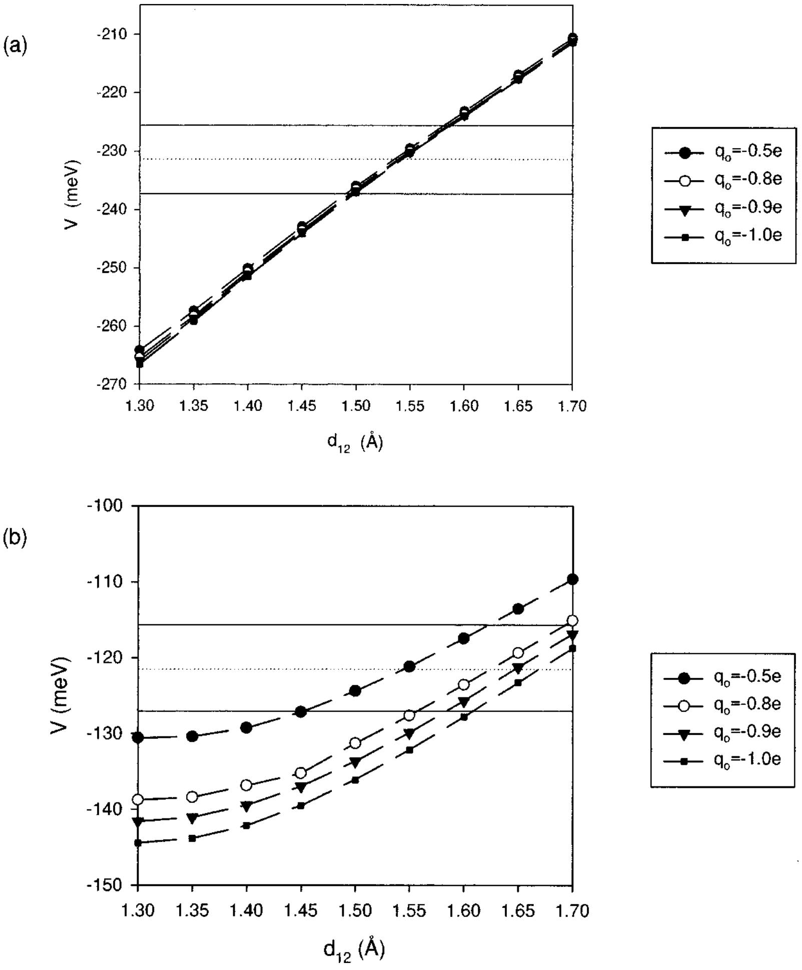

FIG. 3. Variation of the adsorption energy per molecule as a function of the interlayer spacing d_{12} for the Xe monolayer (a) and for the N_2 monolayer (b). The different curves correspond to charge-transfer values q_O equal to $-0.5e$, $-0.8e$, $-0.9e$, and $-1.0e$, respectively. The horizontal lines indicate the experimental values obtained from thermal-desorption spectroscopy (dotted lines), with error bars corresponding to the experimental accuracy of ±6 meV (solid lines).

Smaller ($|q_O|<0.5e$) or larger ($|q_O|>1.0e$) values for the charge transfer are clearly irrelevant since they would correspond to unphysical d_{12} values.

IV. DISCUSSION

Examination of Eqs. (6) and (7) shows that the values which best fit the data are

$$d_{12}=1.60\pm0.05\ \text{Å}, \tag{8}$$

with an ionic charge on the oxygen atom equal to

$$q_O \simeq -(0.8\pm0.2)e. \tag{9}$$

From Eq. (1), the corresponding value of d_O is

$$d_O=-0.21\pm0.10\ \text{Å}. \tag{10}$$

In this model, the distance between the first two Cu planes is expanded by about 0.32 Å as compared to the bulk distance $d_b=1.28$ Å [Fig. 1(b)]. This result is fully consistent with most of the experimental data, where the mean value[20,27] is 1.54 ± 0.06 Å. The negative sign for the resulting value of d_O [Eq. (10)] indicates that the oxygen atoms lie *below* the first Cu plane. The value given by Eq. (10) is larger (in absolute size) than the average of the experimental values, equal to -0.09 ± 0.14 Å, but it should be noted that values as large as -0.34 Å have been determined from x-ray-diffraction data.[15] These values of d_{12} and d_O are quite different from the results of the calculations based on the local-density approximation[27] which give $d_{12}=1.32$ Å and $d_O=0.55$ Å, i.e., an oxygen position above the first Cu plane. *Ab initio* molecular-orbital cluster model calculations[28] obtain $d_O=0.31$ Å if surface reconstruction and relaxation are not allowed, and $d_O=-0.76$ Å if the neighboring Cu atoms are allowed to relax ($d_{12}=2.25$ Å). Although this latter approach is too rough to provide a reliable estimate of the surface relaxation, it probably gives a much better account of the nature of the interaction between the oxygen and surface copper atoms. In particular, it shows that the interaction is highly ionic leading to a charge transfer of about one electron. This value is in very good agreement with the best-fit ionic charge q_O in Eq. (9).

In summary, we have determined reliable values for d_O, d_{12}, and q_O to characterize the oxygen-induced reconstruction of the Cu(110) surface. These values obviously depend on the accuracy of the interaction potential between the adsorbate and substrate. Indeed, this potential must account for the corrugation experienced by the adsorbate to recover the experimental monolayer geometry, and it must give the experimental value of the adsorption energy. The reliability of the coefficients of this potential has been tested for the unreconstructed clean Cu(110) substrate,[2,4,5] and we expect that the lateral interactions are well described, since these are related to the well-known polarizabilities and multipolar moments for Xe and N_2. Regarding the assumptions on the reconstruction, the consideration of the second and third plane relaxation could slightly change the proposed values, but there is experimental evidence for this relaxation to be small. Besides, the lateral displacement of the Cu surface atoms could also affect the geometry of the Xe and N_2 adlayers. These displacements have been disregarded here, since the experiments reveal that they are vanishingly small. Within these weak limitations, the sensitivity of the adsorption properties (structure and binding energy) to the substrate geometry seems to be a strong argument in favor of the proposed values for the parameters d_O, d_{12}, and q_O. The relatively large error bars for d_O and q_O values could be reduced by reducing the interval given in Eq. (7). Improvement of this accuracy could be obtained after considering other molecular adsorbates, such as polar molecules which should be still more sensitive to the oxygen charge. Extension of this approach to other reconstructed substrates (including NiO, AgO, etc.) could be done, but this would require preliminary information on the relationship between d_{12} and d_O. Presently, it seems that these other substrates have not been studied so intensively.[1]

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