Surface as a Foundation to Realizing Designer Materials*

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We entered the 21st Century witnessing several remarkable progress in Science and Technology. Novel materials and devices once considered stuffs of science fiction are, one after another, becoming reality. It would not be an exaggeration to say that we are coming to the Age of Designer Materials — Functional materials that have many varied and competing ground states, allowing us to switch the specific properties using external stimuli, e.g., heat, pressure, electric field, and magnetic field. Here, we present some non-traditional theoretical views developed in our group. The unifying themes are: quantum effects, complexity and functionality. We emphasize the unique role played by the Surface/Interface for providing a special environment (a foundation) for realizing Designer Materials, that are not realizable in the bulk and the strategic choice of particular elements as building blocks, e.g., for Exhaust Purification, Memory Devices and (Nano) Spintronics Applications. [DOI: 10.1380/ejssnt.2014.203]

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I. INTRODUCTION

We entered the 21st Century witnessing several remarkable developments in Science and Technology. Novel materials and devices that were once considered science fiction materials are now, one after the other, becoming a reality. On the other hand, as is always the case, progress comes at a price. In the process of the continuing progress in Science and Technology, we encounter new problems and phenomena where conventional techniques and routines no longer apply. In particular is the astonishing development seen in nanometer scale technology, a domain we now call as Nanotechnology. To meet the ever-increasing demand for better large-scale integration, basic components of devices are getting smaller, with the size ranging from the nanometer-scale to atomic-scale level. With this, one can easily realize that Quantum Effects are becoming more important. (We are currently in the stage of discovering the significance of Quantum Effects in the field of Nanotechnology.) However, it is not an exaggeration if we say that, with further development, there will come a time when the basic material entity now used to build a device would be developed to function as a device itself. Given these circumstances, there will be high demands and necessities in developing novel theoretical routines and techniques that could quickly and efficiently find novel materials for synthesis that would suit our objectives. These necessary theoretical routines and techniques should incorporate quantum mechanics per se and should not be dependent on experimental results and/or empirical parameters. Ab-Initio/First Principles Calculations satisfy all these requirements.

With recent developments in computational techniques, coupled with the rapid progress in terms of efficiency and computational capability of present computers, ab-initio/first principles-based COMPUTATIONAL MATERIALS DESIGN (CMD®) [1] is now a reality. Its impact/influence on industrial R&D is becoming very significant and will increase in succeeding years. It is worth mentioning that there are already several precedents of patents granted for application based purely on the application of CMD® techniques [1–3] and more are expected to follow.

II. COMPUTATIONAL MATERIALS DESIGN (CMD®)

The key concept behind Computational Materials Design (CMD®) is Quantum Mechanical Analysis. Quantum mechanical analysis entails treating the interaction of the many electron system, and using these interactions to determine the different properties of the material, as well as predict changes upon interaction with other materials, without the use of empirical data (i.e., data derived from experimental results). This concept has already been employed in our group’s early studies on molecule-metal surface interaction. In early studies involving H adsorption on metal surfaces, using a simple model Hamiltonian [4], essential parameters like nearest neighbor transfer matrix element $t$ and Coulomb interaction energy $U$ in the substrate, as well as the transfer matrix element $V$ between the adatom and the surface were investigated. Considering these parameters, it was determined that the interaction between the adatom and the metal surface is of local character, such that the effects would be prominent on small surface clusters. Furthermore, the parameter $U/|t|$ was found to give us a measure of the strength of H atom binding with the metal surface and, with that,
FIG. 1: Process of designing material structures employing Computational Materials Design (CMD®) techniques. CMD® is described in comparison with the previous method of explaining experimental results.

the predictive power to determine what kind of surface material will provide stronger H-metal surface binding. Thus, one could distinguish a transition-metal-like surface from a simple-metal-like surface. This method of materials design was extended to early studies on dissociative chemisorption of H₂ on metal surface [5] wherein, using Hubbard’s second approximation, it was determined that the value of the critical parameter \( V_C \) to determine H₂ dissociation, is dependent on the previously known parameter \( U/|t| \). Thus, this computational method was shown to be a powerful technique for materials design and applications/studies were extended to quantum dynamical calculations of larger molecules, such as NO scattering on a metal surface such as Ag (111) [6]. Different parameters were investigated to determine the effect on the final rotational state distribution of NO scattered from Ag (111) surfaces and the theoretical results could still be improved by varying further the parameters of the model. From this investigation, results show the importance of having the correct value of the well depth to fit the rotational state of NO to a rigid rotor scattered by a rigid flat surface and the weak linear dependence of the rotational state maxima on the incident energy normal to the surface. Further improvements to the theoretical description were suggested, e.g., by considering surface corrugation. Eventually, with these benchmark systems, progress in materials design enabled surface science-based reaction design, e.g., as applied to studies on ortho-para hydrogen conversion, with the purpose of increasing conversion yield via molecular orientation [7].

Understanding the properties of materials with different intended purpose could pave the way for materials engineering through simulations done even before going through expensive experimental trials. A very important computational technique governed by this is First Principles Calculations or Ab Initio Calculations, where Density Functional Theory (DFT) has proven to be one of its most powerful and useful tool [8]. Recent developments in computational techniques, coupled with the rapid progress in computer efficiency, make ab-initio/first principles-based CMD® a relevant field in the world of surface science and condensed matter physics [9]. Its application has been used in a wide variety of simulation codes that could very well provide results comparable with that obtained from experiments. This leads to the development of novel materials in the field of nanotechnology, where advances in material science provide improvement in areas such as solar cells, nanofibers, sensors and ultra light materials. Some recent applications of CMD® on fuel cell technology are on studies related to finding potential alternatives to the very expensive platinum, commonly used as a catalyst at the electrodes of the fuel cell [10, 11]. The CMD® process that is originally developed by our group is shown in Fig. 1. Basic understanding of a physical system is obtained by theoretical means, e.g. quantum dynamical calculations and/or first principles calculations. Equipped with these understanding, parameters that are relevant to the proposed purpose can be altered so as to obtain a new and functionalized material. Materials testing could then be done by experimentalist to verify the physical feasibility of the proposed new material. The results obtained from these steps will then be used to further improve the initially proposed material and/or device another material derived from the basic understanding obtained from materials design. In this cyclic process, good collaboration with experimental investigators is imperative provide efficient results.

III. NANIWA SERIES

Modern computational techniques at the quantum level entail appropriate codes that could very well handle/represent the system. Naniwa-series is a computational code for performing first principles quantum dynamics calculations. As the description implies, it is a quantum mechanical version of classical molecular dynamics (MD) calculations. A classical description of the system involved in, e.g., surface reactions (dissociative scattering, molecular scattering, dissociative adsorption,
associative desorption, etc.), can be used, when quantum effects, such as tunneling, diffractions and electronic excitations, play no essential role in the dynamics. In addition to this, the kinetic energy of, e.g., the impinging particle must be large enough, to ensure that the de Broglie wavelength is much smaller than the lattice constant of the solid (typically of the order of a few Ångström), to be able to neglect interference phenomena. For hydrogen, with a translational energy of say 20 meV, the de Broglie wavelength is a few Ångström. This dictates that we treat hydrogen as a quantum particle. For all the relevant surface reactions, there is a strong interaction between the impinging particle and the surface. This compounds the situation because interactions imply coupling between the internal degrees-of-freedom (e.g., vibration, rotation and translation) of the particles immediately involved in the reaction. The vibrational motion requires a quantum description, esp., when the respective quanta are large. Thus, the coupling between the internal degrees-of-freedom also requires a quantum mechanical description. As one would expect, this computation code could also handle such problems as quantum transport and quantum scattering in general. For the first principles quantum dynamics calculation done by Naniwa-series can be broken down into two main stages, viz.,

1. A DFT based determination of the effective potential energy (hyper-) surface (PES) governing the reaction [8].

2. Solution of the corresponding multi-dimensional Schrödinger equation for the reaction described by the above-determined PES, based on coupled-channel method [12, 13] and the concept of local reflection matrix [14].

For a more detailed discussions on the basics and application of Naniwa-series, we introduce in the next session IV.A.

IV. CASE STUDIES

A. Fundamental Research of Molecular-Surface Reaction [1, 2, 13]

Diatomic molecules generally have a preferential orientation of molecular axis for adsorption on metal surfaces. Molecules such as CO and NO are bound molecularly at several metal surfaces with the molecular axis oriented perpendicularly to the surfaces. The orientation for CO and NO is such that the C or N is the binding atom [15, 16]. These are typical examples of the molecular adsorption system.

On the other hand, hydrogen molecules and many other molecules, adsorb dissociatively on noble or transition metal surfaces. In this case, the orientation of the molecular axis parallel to the surface is considered to be more preferential for dissociative adsorption than the orientation perpendicular to the surface [15, 17–19]. Molecules generally suffer from a confining potential depending on the orientation of molecular axis near surfaces. Then, it can be considered that the initial rotational energy of the molecules may prevent the molecules from sticking onto the surfaces, because the initial rotational energy may prevent the molecular axis from being arranged in the preferential orientation for adsorption. In other words, the initial rotational energy may produce an effective barrier for adsorption.

As for the desorption process from the surfaces, assuming the detailed balance relation between the adsorption and desorption processes, that the desorption probability $D_i$ of molecules finally in the $l$-th internal state is proportional to $S_l$, $S_l$ denotes the sticking probability of the molecules initially in the $l$-th internal state, i.e., $D_i \propto S_l \exp(-E_i/k_BT_s)$. $E_i$ denotes the energy relevant to the $l$-th internal state and $T_s$ the surface temperature [20, 21]. If we consider the rotational state as the internal state, then, the rotational excitation probability of desorbing molecules becomes smaller than that expected from the Boltzmann distribution at $T_s$, because $S_l$ is generally considered to be a decreasing function of $E_i$. Thus, one can expect that rotational cooling is a general phenomenon in desorption for both molecular and dissociative adsorption systems.

The rotational cooling phenomenon in the desorption process of the molecular adsorption system has been observed experimentally [22–24] and explained theoretically [20, 25]. Rotational cooling has been observed in the associative desorption process of dissociative adsorption systems [26–28].

As for the vibrational excitation of thermally desorbing molecules, vibrational cooling has been observed in the desorption of NO from Pt(111) [29]. That is, the vibrational excitation probability of desorbing NO is smaller than that expected from the Boltzmann distribution at $T_s$. The experimental results have been well reproduced by calculations based on the kinetic theory of gas molecule-surface scattering [21, 30]. On the other hand, vibrational heating has been observed in the associative desorption process of hydrogen from Cu and Pd surfaces [26–28]. This means that the vibrational excitation probability of associatively desorbing hydrogen is larger than that expected from the Boltzmann distribution at $T_s$. Vibrational heating in the associative desorption process has been reproduced by calculations based on the concept of a reaction path, where the rotational degree of freedom has been neglected for simplicity [12, 31]. Here, the vibrational excitation of hydrogen molecules interacting with metal surfaces is determined within a simple model in which the rotational degree-of-freedom is taken into account, together with the vibrational one [13].

The Hamiltonian used to describe the dynamics of a hydrogen molecule interacting with a metal surface is given as an extension of the model Hamiltonian [12].

$$H = H_0 + H_1,$$

$$H_0 = -\frac{\hbar^2}{2\mu} \frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{2\mu} \frac{1}{2l(s)} \left( \frac{\partial}{\partial \theta} \left( \frac{\sin \theta}{\sin \theta} \frac{\partial}{\partial \theta} \right) + \frac{\partial^2}{\partial \phi^2} \right) + V(r, \theta, \phi, s)$$

and

$$H_1 = -\frac{\hbar^2}{2\mu} \left[ \frac{r_0(s)}{r - r_0(s)} \right]^2 \frac{\partial^2}{\partial s^2}.$$

http://www.sssj.org/ejsnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsnt/)
r denotes the vibrational coordinate. s denotes the reaction path coordinate. \( \theta \) denotes the angle of molecular axis with respect to the surface normal, and \( \phi \) the azimuthal. Far from the surface, \( r \) represents the distance between the two nuclei of the molecule and \( s \) the distance of the molecular center-of-mass from the surface. At distances near the surface, \( r \) represents the distance of the center-of-mass of the two nuclei from the surface and \( s \) the distance between the two nuclei of dissociatively adsorbed atoms. \( \mu \) and \( I(s) \) are the reduced mass and the moment of inertia of the molecule, respectively. The last term on the right-hand side of the equation (2) represents the potential energy surface relevant to the present system. \( \kappa(s) = [r_0(s)]^{-1} \) is the curvature of the reaction path. The \( s \) dependence of \( \kappa(s) \) is assumed to be given by [30]

\[
\kappa(s) = \frac{1}{\varphi_0(s)} = \frac{1}{\varphi_0(\cosh^{-1}\lambda(s - s_0))}.
\]

The \( s \) dependence of \( I(s) \) is tentatively assumed to be given by

\[
I(s) = I(+\infty) \frac{2}{1 + \tanh[\lambda(s - s_1)]}.
\]

If we assume the surface to be flat, for simplicity, the potential becomes independent of the azimuthal angle \( \phi \). The potential then take the form

\[
V(r, \theta, \phi, s) \simeq V_0(r) + V_1(\theta, s).
\]

The first term represents the potential for the vibrational motion (Morse potential relevant to the intramolecular potential for the molecule in the gas phase) [12]. The second term is a diagonal potential with respect to the vibrational motion (in principle including the zero point vibrational motion), of which the maximum value corresponds to the activation barrier for the reaction (the associative desorption and the dissociative adsorption in the present case). \( V_1(\theta, s) \) is given by

\[
V_1(\theta, s) \simeq \tilde{V}_1(s) + \beta \tilde{W}_1(s) P_2(\cos \theta),
\]

where \( P_2 = (3\cos^2 - 1)/2 \).

\[
\tilde{V}_1(s) = E_0 \cosh^{-2} \lambda s
\]

and

\[
\tilde{W}_1(s) = E_c (1 - \tanh \lambda s)/2 + \tilde{V}_1(s).
\]

The \( \theta \) dependence of \( V_1(\theta, s) \) is chosen such that, near the surface the orientation of molecular axis parallel to the surface becomes preferential over the orientation of molecular axis perpendicular to the surface. Parameters used in the following calculations, relevant to H\(_2\)-Cu system, are summarized in Table I [12, 30]. Because of the small mass ratio \( M(H_2)/M(Cu) \), one can neglect the energy transfer to the surface phonon system from the molecule, as a first approximation [32].

In Fig. 2, we show, the rotational state distribution of associatively desorbing hydrogen molecules which are finally in the first-excited vibrational state, for the surface temperature \( T_s = 850 \) K. Here, the desorption probability of the molecules, which are finally in \((l, m)\) rotational and \(\nu\)-th vibrational states, from the surface at \( T_s \) is given in terms of \( D_{l,m,\nu,l',m',\nu'} \) as follows:

\[
N_{l,m,\nu} = \int_0^{+\infty} \sum_{l',m',\nu'} |D_{l,m,\nu,l',m',\nu'}(E)|^2 \exp(-E/k_B T_s) dE/(k_B T_s).
\]

As one can see in the figure, the rotational excitation probability is smaller than that expected from the Boltzmann distribution at \( T_s \). That is, rotational cooling occurs in the associative desorption process. In accord with the experimental observation [26], the rotational state distribution exhibits practically the same pattern for the molecules in the ground and first-excited vibrational states. Rotational cooling can be seen as well for desorbing molecules in the ground vibrational state.

In Fig. 3, we show the desorption probability of the molecules which are finally in the rotational state of the same quantum number of total angular momentum with different magnetic quantum numbers. As follows from the figure, the desorption probability is larger in general for the molecules in the rotational states with a larger absolute value of magnetic quantum number \( |m| \). This means that the rotational motion of desorbing molecules is of helicopter type rather than of cartwheel type [33]. On the basis of the detailed balance relation mentioned in the introduction, it is anticipated that, if the rotational energy is the same, the sticking probability is larger for the molecules with helicopter type motion. It is interesting to check this experimentally.

The vibrational excitation probability takes the value of 3.4% at \( T_s = 850 \) K for the set of parameters used here. Within the given experimental error bars, this value agrees with the experimental one [26] and is almost two orders of magnitude larger than that (\( \sim 0.05\% \)) expected from the Boltzmann distribution at \( T_s \). The vibrational heating in desorption is reproduced by the present calculations on the basis of the model in which the rotational
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FIG. 2: The rotational state distribution of associatively desorbing hydrogen in Boltzmann plot, \( \ln|\sum_{m=-l}^{l} N_{l,m,\nu}/(2l+1)| + \text{const.} \) vs rotational energy. Solid line is for the molecule finally in the first-excited vibrational state at \( T_s = 850 \) K. The dash-dotted line corresponds to the case if the rotational state distribution is the same as the Boltzmann distribution at \( T_s \). From [13].

FIG. 3: The desorption probability \( \sum_{l',m',\nu'} |D_{l,m,\nu;l',m',\nu'}|^2 \) of the molecule finally in \( (l,m,\nu) = (5,0,0) \) state (solid line) and in \( (5,5,0) \) state (dashed line) as a function of the translational energy. From [13].

as well as the vibrational degrees of freedom are taken into account.

In Fig. 4, we show the sticking probability as a function of translational energy for the molecules initially in the ground and first-excited vibrational states. In accord with the experimental observations [16, 17], vibrationally assisted sticking occurs, i.e., the sticking probability of particles initially in the first-excited vibrational state is considerably enhanced as compared to those in the ground state [12, 31].

In Fig. 5, we show the sticking probability as a function of translational energy for the molecules initially in different rotational states. That is, the initial rotational energy prevents the molecules from sticking onto the surfaces. This phenomenon may be called rotationally hindered sticking, the occurrence of which has been concluded in the molecular adsorption system as well [20, 25].

B. Case Studies of CMD®

We have investigated some applications of CMD®, e.g., enhancing oxygen reduction reaction on spin-polarized metal surface for fuel cell applications [36–40] and surface spintronics device [41, 42]. We have also carried

FIG. 4: Sticking probability as a function of translational energy for the molecule initially in \( (l,m,\nu) = (0,0,0) \) state (dashed line) and in \( (0,0,1) \) state (solid line). From [13].

FIG. 5: Sticking probability as a function of translational energy for the molecule initially in \( (l,m,\nu) = (0,0,0) \) state (solid line) and in \( (5,0,0) \) state (dashed line). From [13].

FIG. 6: The optimized structures of (a) Cu(111), (b) O-terminated Cu2O(111) and (c) Cu-terminated Cu2O(111) surfaces. The gray and red spheres represent Cu and O atoms, respectively. The notation used for the surface Cu atoms of the Cu2O(111) surfaces corresponds to the arrangement of the atoms in the unit cell. The triangular dashed lines represent the three-fold sites for the Cu2O(111) surfaces. From [55].
We introduce some topics of CMD useful for designing novel surface spintronics application. This fundamental research on magnetism control is Kondo effect and influence of the RKKY interaction. From fundamental research, e.g., real space image of the spin-down electrons, respectively. From [55].

Negative values of the vertical axis correspond to spin-up and to the surface atoms as defined in Fig. 6. The positive and Cu$_2$O(111), (b) O-terminated Cu$_2$O(111) and (c) Cu-terminated Cu$_2$O(111) surfaces. The legends in each figure correspond to the surface atoms as defined in Fig. 6. The positive and negative values of the vertical axis correspond to spin-up and spin-down electrons, respectively. From [55].

out fundamental research, e.g., real space image of the Kondo effect and influence of the RKKY interaction. This fundamental research on magnetism control is useful for designing novel surface spintronics application. We introduce some topics of CMD, e.g., the application research of catalyst for exhaust gas purification and memory devices and the fundamental research of magnetic anisotropy of magnetic multilayer.

1. Precious Metal Free Catalyst for Exhaust Gas Purification [54, 55]

Reduction of NO$_x$ is a major research topic at present [56–68]. NO$_x$, which is a by-product of fossil fuel combustion, basically forms nitric acid in air, which is the main reason for acid rain and smog. This alarming issue needs to be addressed by both the automobile industry and the scientific community.

The NO$_x$ reduction process on precious metal, e.g., Pd, Pt and Rh, surfaces has been already investigated [56–61]. Nevertheless, the employment of these metals as catalysts is hindered by their high cost. Therefore, we would like to find more inexpensive materials with comparable catalytic performance to those of the precious metals towards NO$_x$ reduction.

We previously investigated the dissociation of NO on Cu(111) and Cu$_2$O(111) surfaces [69]. On Cu(111), NO dissociation is accompanied by a high activation barrier and desorption is more likely to happen. On Cu$_2$O(111), we found that the reaction path for NO dissociation is an exothermic process and does not require extra energy for the dissociation (with reference to the energetics of isolated NO and a Cu$_2$O(111) surface). The reaction path of NO on Cu$_2$O(111) is comparable to that observed for the case of the NO-Rh system [67].

Here, we compare the geometric and electronic structures of Cu(111) and Cu$_2$O(111) systems using DFT [55]. Understanding of this will be beneficial for the realization of a cheap catalyst for NO$_x$ reduction.

Figure 6 shows the optimized structures of the Cu(111), O-terminated Cu$_2$O(111) and Cu-terminated Cu$_2$O(111) surfaces. From the figure, the Cu(111) surface maintains its closed-pack arrangement and no significant relaxation occurred on the plane parallel to the surface (Fig. 6(a)). However, it is observed that the relaxation of the surface atoms of the Cu$_2$O surface is very evident as the Cu atoms tend to position themselves with reference to the O atom. In particular, a well-defined three-fold site is observed with reference to the O atom on the surface for the case of O-terminated Cu$_2$O (Fig. 6(b)). The same phenomenon happened for the case of a Cu-terminated surface, but in this case a three-fold site is perceived due to the presence of O on the subsurface (Fig. 6(c)). The three-fold sites are marked by dashed lines in Fig. 6. This resembles the rounded pyramidal shape of the Cu atoms observed experimentally using scanning tunneling microscope (STM) by Östuen et al., [70].

Next, we investigated the local density of states (LDOS) of the d-orbital of the surface Cu atoms, shown in Fig. 7. The DOS of Cu in the Cu(111) reflects the filled d-orbital of the atom. For the case of a Cu$_2$O surface, the surface Cu atoms of the Cu-terminated and O-terminated surfaces exhibit almost the same DOS profile. The states are shifted towards the Fermi level, $E_F$, which is a consequence of the interaction of the Cu atoms with the O atom. For the case of an O-terminated system, the shifted peaks appear at around $-1.0$ eV with reference to the $E_F$, whereas, the shifted peak for the case of the Cu-terminated surface appears at about $-0.5$ eV. We conclude that the difference in the shifting is due to the different environment that the surface Cu atoms experience on both surfaces. It can be noted that an O atom is present on the surface and on the subsurface for the case of O-terminated Cu$_2$O, while only O atoms appear on the subsurface for the case of Cu-terminated Cu$_2$O. Furthermore, the occurrence of a peak in the region of unoccupied states is an indication of charge transfer from the Cu atoms to the O atoms.

As we observed that the DOS of the d-orbital of the...
For all cases, 

energy, \( E \), affects the possibility of dissociation. The adsorption 

configuration of NO on the surface is dictated by the weakening of 

the NO bond when it is adsorbed on the surface. In relation to our work, we claim that the capability of the surface Cu atoms to hybridize with the NO molecule greatly affects the possibility of dissociation. The adsorption energy, \( E_{\text{ads}} \), of NO and its bond length as it is adsorbed on the surface are presented in Table II. For all cases, NO is molecularly adsorbed on the three-fold site. Although states are also present in the region along the \( E_F \) for the case of an O-terminated surface (Fig. 7(b)), these states are already interacting with the O atoms on the surface and subsurface. Thus, it can be claimed that this scenario limits the surface Cu atoms to actively hybridize with the approaching NO molecule, unlike for the case of a Cu-terminated surface.

A high activation barrier on Cu(111) is found due to the inability of Cu atoms, having a filled \( d \)-orbital, to interact with NO. For the case of an O-terminated Cu\(_2\)O surface, NO adsorption is possible but dissociated N and O atoms are found to be unstable due to passivation of the active sites (three-fold sites) by the O atoms on the surface; thus a very large activation energy is expected. For the Cu-terminated Cu\(_2\)O system, since states are present around the region of the \( E_F \), Cu atoms can participate in the charge donation process that weakens the NO bond. By this phenomenon and with the presence of available hollow sites, O can be easily detached from the NO molecule and become stable on the Cu-terminated Cu\(_2\)O surface as isolated N and O atoms.

Although the calculations performed in this study are for the ground state, the results obtained are in good agreement with our initial experimental findings. Here, we note a 98.3% NO conversion on Cu\(_2\)O under a reducing atmosphere, whereas only 5.7-23.6% is attainable for other oxide surfaces. Our analyses support the high

surface Cu atoms in the Cu\(_2\)O surfaces is shifted towards \( E_F \), we constructed the charge density distribution of the surfaces in the region along \( E_F \) (between \(-0.5 \text{ eV and } E_F \)) as shown in Fig. 8 with an isosurface value of 0.02 e\(^{-3}\). Two-dimensional (2D) views of the charge distribution that slices the surface plane are also illustrated. In Cu(111), in the vicinity of \( E_F \), the charge distribution is localized to its respective atoms as there are a small number of states in the region. The distribution for the case of an O-terminated Cu\(_2\)O(111) surface is also somehow localized to the respective atoms, as shown in Fig. 8(b), although the distribution extends further into the space as seen by the presence of states along that region. However, for the Cu-terminated Cu\(_2\)O surface, the charge distribution extends along the area of the three-fold site, which is a consequence of the appearance of a peak at about \(-0.5 \text{ eV} \) as identified from the LDOS. From this, it can be assumed that the three-fold site is an active site of the surface in such a way that charges are present in the site that can participate in the bonding process. As mentioned earlier, [70] predicted that unsaturated Cu ions exist on the Cu\(_2\)O(111) surface. They stated that such an interpretation is reasonable as the broken bonds could leave additional charges on the Cu ions resulting in the bright regions. Their result is in agreement with the charge distribution we obtained for the case of Cu-terminated Cu\(_2\)O(111) as these bright regions correspond to the charge distribution in the area of the three-fold site (Fig. 8(c)) which is the active site for NO adsorption in our work.

We stated in our previous work [69] that the dissociation of NO on the surface is dictated by the weakening of the NO bond when it is adsorbed on the surface. In relation to our work, we claim that the capability of the surface Cu atoms to hybridize with the NO molecule greatly affects the possibility of dissociation. The adsorption energy, \( E_{\text{ads}} \), of NO and its bond length as it is adsorbed on the surface are presented in Table II. For all cases, NO is molecularly adsorbed on the three-fold site. Although states are also present in the region along the \( E_F \) for the case of an O-terminated surface (Fig. 7(b)), these states are already interacting with the O atoms on the surface and subsurface. Thus, it can be claimed that this scenario limits the surface Cu atoms to actively hybridize with the approaching NO molecule, unlike for the case of a Cu-terminated surface.

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**TABLE II: Bond length of the adsorbed NO molecule on the surfaces and the corresponding adsorption energies (\( E_{\text{ads}} \)).** From [55].

| Surface                     | Bond length (Å) | \( E_{\text{ads}} \) (eV) |
|-----------------------------|-----------------|----------------------------|
| Cu(111)                     | 1.22            | 0.92                       |
| O-terminated - Cu\(_2\)O(111) | 1.19            | 0.98                       |
| Cu-terminated - Cu\(_2\)O(111) | 1.28            | 1.56                       |

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**FIG. 8: Partial charge density distribution and its corresponding 2D view that slices the surface plane of (a) Cu(111), (b) O-terminated Cu\(_2\)O(111) and (c) Cu-terminated Cu\(_2\)O(111) surfaces evaluated at an energy range between the Fermi energy and at a value of \(-0.5 \text{ eV} \), with an isosurface value of 0.002 e\(^{-3}\). The directions of the lattice vectors are shown and the three-fold sites are represented by the triangles which are also identified in Fig. 6. The gray and red spheres represent Cu and O atoms, respectively.**
reactivity of Cu$_2$O surfaces towards NO$_x$ reduction. The performance of Cu$_2$O is comparable to Rh, since both of these materials were previously shown to have similar characteristic reaction paths for NO dissociation wherein both are exothermic.

2. A Step Closer Towards Commercialization of Next-Generation Memory Devices [71, 72]

Flash memories are presently widely used as nonvolatile memories for secondary storage, or long-term persistent storage. However, in order to improve the performance, e.g., speed and/or number of rewritings, research on next generation nonvolatile memory devices is becoming increasingly vigorous. In particular, studies on resistance random access memories (RRAMs) [73-79] have become intensive because of their superior properties for achieving lower power consumption, larger-scale integration and higher speed. RRAM is designed to change the resistance of transition metal oxides (TMOs) via the application of a sufficiently high voltage [80]. However, the switching mechanism is not completely clarified. Therefore, it is necessary to elucidate the factors related to the changing resistance of the RRAM.

Some studies related to RRAM suggest that the creation of oxygen vacancies and charge carrier trapping might be responsible for the switching mechanism [81-84] and report that the behavior of RRAM materials near the anode plays an important role in the switching mechanism [85]. Meanwhile, our coworkers have investigated the oxidative reaction in the vicinity of the anode through experimental and theoretical approaches [86]. We have investigated the electronic states of TMO-anode interfaces both in the electrode layers and TMO layers [87, 88]. However, the effects of roughness (e.g., oxygen vacancies) and charge carrier trapping have not been clarified yet. Here, by performing first-principles calculations based on the DFT, we analyze the properties of the TMO layers with oxygen vacancies and the effect of charge carrier trapping in the vicinity of the oxygen vacancies on the electronic properties [72]. In addition, we discuss the suitability of electrode materials by comparing the results for Ta, W and Pt.

First, we consider the properties of bulk CoO without oxygen vacancies. Bulk CoO is known to have antiferromagnetic properties. We use the supercell represented in Fig. 9 with the lattice constant of 4.26 Å [89]. The resulting DOS is shown in Fig. 10(a).

Second, we consider the properties of bulk CoO with oxygen vacancies. We analyze the structure by removing one oxygen atom, which corresponds to defect concentrations of 6.25%, from a supercell, as indicated in Fig. 9. The most stable structure is obtained by the relaxation of all atoms. We find that the formation energy of an oxygen vacancy requires 4.894 eV by comparing the stabilities of bulk CoO without and with oxygen vacancies. The DOS of bulk CoO with oxygen vacancies is shown in Fig. 10(b).

Finally, we perform a calculation for bulk CoO with oxygen vacancies by adding an extra electron per supercell as a reference for charge carrier trapping. The DOS for the charged case is shown in Fig. 10(c).

The DOS of bulk CoO without oxygen vacancies, as shown in Fig. 10(a), exhibits a large bandgap around $E_F$, which indicates that bulk CoO is an insulator. The DOS of bulk CoO with oxygen vacancies in Fig. 10(b) shows a shift in the energy level and a small structure around $E_F$.

Moreover, the DOS of bulk CoO with oxygen vacancies and charge carrier trapping in Fig. 10(c) manifests a certain structure around $E_F$. The results of these calculations indicate a change in the property of the bulk CoO from insulating to metallic through oxygen vacancies and charge carrier trapping. Moreover, we analyze the DOS
FIG. 11: LDOS on Co atoms (a) near and (b) far from oxygen vacancies. From [72].

FIG. 12: Band structure of bulk CoO with oxygen vacancies and charge carrier trapping. From [72].

FIG. 13: Slab model of CoO layers in contact with an electrode layer depicted in the same manner as Fig. 74. The black circles represent atoms of the electrode. From [72].

FIG. 14: LDOS at each CoO layer in the case of the Ta electrode: (a) first, (b) second, and (c) third CoO layers. From [72].

of the Co atom near the oxygen vacancy [Co atom (a) in Fig. 9] and the Co atom far from the oxygen vacancy [Co atom (b) in Fig. 9] in order to analyze the electron state distribution that represents the metallic property. The results show that Co atom (a) has electron states around \( E_F \) [Fig. 11(a)] whereas Co atom (b) does not [Fig. 11(b)]. This indicates that Co atoms near the oxygen vacancies become metallic [90].

We also analyze the band structure of bulk CoO with oxygen vacancies and charge carrier trapping (Fig. 12) [91]. By this analysis, we also confirm the electrical conductivity of bulk CoO with oxygen vacancies and charge carrier trapping [92]. Additionally, we perform calculations for a slab model consisting of 4 CoO layers in contact with an electrode layer in order to consider the effect of oxygen vacancies and charge carrier trapping at the interface between the CoO layer and the electrode layer. We analyze Ta, W and Pt electrodes on CoO(001). The slab model for the Ta electrode is shown in Fig. 13. We have confirmed that Ta and W stably adsorb on the top sites on the oxygen atoms and Pt at the hollow sites. The DOS of different CoO layers for Ta, W and Pt electrodes are shown in Fig. 14, 15 and 16, respectively. From Figs. 14 and 15, we find that the first layer of CoO is metallic and the lower layers of CoO are insulating. From Fig. 16, we find that the first and second layers of CoO are metallic and...
We also consider the properties of the CoO slab with an oxygen vacancy, which corresponds to defect concentrations of 6.25%, per supercell at the first or second layer of CoO in order to analyze the effects of oxygen vacancies at the interface between the CoO layer and the electrode layer. We analyze the charged state of each model with oxygen vacancies at the first layer of CoO by increasing the number of valence electrons. The results show that all layers that are initially insulating remain insulating. The comparison of the DOS for the second layer of CoO in contact with the Ta electrode is shown in Fig. 17. The results show that oxygen vacancies near the electrode layer have no effect on changing the insulating properties of CoO layers to metallic. Moreover, we analyze the charged state of each model with oxygen vacancies at the second layer of CoO by increasing the number of valence electrons. The results show that the second layer that is initially insulating changes to metallic. The comparison of the DOS for the second layer of CoO in Fig. 18. The results show that oxygen vacancies apart from the electrode layer have an effect on changing the insulating properties of CoO layers to metallic.

On the basis of the above results, we can explain the switching mechanism of RRAM by assuming that oxygen vacancies connect the conduction path to the electrode through the migration of oxygen vacancies from the interface to lower layers of CoO. In the case of the high-resistance state depicted in Fig. 19(a), an oxygen atom interrupts the conduction path between interface and lower layers. The application of voltage induces the migration of the oxygen atoms in CoO toward the interface. Then, in the case of the low-resistance state depicted in Fig. 19(b), the oxygen vacancies connect the conduction paths between the anode and the cathode and hence the RRAM device becomes conductive.

Moreover, we evaluate the properties of the CoO slab in contact with Ta, W and Pt electrodes in order to investigate the effects of oxygen vacancies at the interface between the CoO layer and the electrode layer. The formation energies of oxygen vacancies for different kinds of electrodes are shown in Table III. The results show that oxygen vacancies are formed favorably at the first layer of CoO in every model. By comparing the results for the slab models without oxygen vacancies, we find that there are more metallic layers below the interface in the case of the Pt electrode than in the cases of Ta and W electrodes. On the basis of the obtained results, we identify the best electrode material from among the three by comparison of the controllability of resistance. In the case of the Pt electrode, the required formation energy of oxygen vacancies is low (1.114 eV) in the first layer of CoO and high (4.074 eV) in the second layer. Since both the first and the second layer are originally metallic without oxygen vacancies, the application of high voltage will be

![FIG. 15: LDOS at each CoO layer in the case of W electrode: (a) first, (b) second, and (c) third CoO layers. From [72].](image1)

![FIG. 16: LDOS at each CoO layer in the case of Pt electrode: (a) first, (b) second, and (c) third CoO layers. From [72].](image2)

![TABLE III: Formation energies of oxygen vacancies at the first and second layers of CoO for each electrons (unit: eV). From [72].](table)

| Electrode | First layer | Second layer |
|-----------|-------------|--------------|
| Ta        | 4.860       | 5.280        |
| W         | 3.208       | 3.672        |
| Pt        | 1.114       | 4.074        |
required to induce a resistance change via the formation of oxygen vacancies in the deep layers. Therefore, Pt will not be a desirable electrode material for RRAM devices. In the case of the Ta electrode, the second layer of CoO is originally insulating and the difference in the formation energy of oxygen vacancies between the first and the second layer of CoO is small; however, the absolute values of the energies are high (4.860 eV for the first layer). Therefore, the application of high voltage will again be required to change the resistance.

In the case of the W electrode, the second layer of CoO is originally insulating and the absolute values for the formation energy of oxygen vacancies in both of the first and the second layer of CoO are small (3.208 eV for the first layer). Since the required voltage to change the resistance will be low, the W electrode is a desirable electrode material compared with Ta and Pt.

3. Electronic and Magnetic Properties of Co/Ni Multi-Layers [93]

Current-induced magnetic domain wall motion in ferromagnetic nanowires has been intensively investigated, not only because of their potential for magnetic random access memory device applications [94–97], but also the interesting electronic properties [98–100] of the ferromagnetic atoms. Recently, interesting experimental results of Co/Ni ultra-thin multi-layers on W(110) were reported [101, 102]. In this system, first, two Ni monolayers (Ni 2ML) are deposited on W(110). Real-time spin-polarized low electron microscope (SPLEEM) image shows that no particular easy magnetization preference of the surface ferromagnetic atoms for Ni 1ML and 2ML on W(110). Upon depositing Co 1ML on this system (Co1ML/Ni 2ML), the SPLEEM image shows that the axis of easy magnetization of the surface ferromagnetic atoms becomes in-plane.

Here, we focus on the following system, Ni 1ML, Ni 2ML and Co 1ML/Ni 2ML on W(110) [93]. First, we analyze why the axis of easy magnetization of the surface ferromagnetic atoms does not exist in Ni 1ML on W(110). Second, we analyze the origin of magnetic anisotropy in Co 1ML/Ni 2ML on W(110).

In Table IV, we show the most stable adsorption site and interlayer distance between surface atomic layer and substrate in Ni 1ML, Ni 2ML and Co 1ML/Ni 2ML on W(110). From [93],

| on W(110)    | site | interlayer distance [Å] |
|-------------|------|-------------------------|
| Ni 1ML      | lb   | 1.8                     |
| Ni 2ML      | lb   | 1.7                     |
| Co 1ML/Ni 2ML | lb  | 1.6                     |

http://www.sssj.org/ejsnt (J-Stage: http://www.jstage.jst.go.jp/browse/ejsnt/)
FIG. 19: Enlargement of the interface between TMO and electrode: (a) high- and (b) low-resistance states of RRAM. The dark gray circles represent oxygen atoms. The center white part represents the conduction path. The light gray part represents the CoO layer that is initially metallic. From [72].

FIG. 20: W(110) surface from [110] direction. Black balls denote W atoms. White lines indicate the unit cell used in the calculation. h, sb, lb and t denote hollow site, short bridge site, long bridge site and top site, respectively. From [93].

TABLE V: The magnetic moment of each atom in Ni 1ML, Ni 2ML and Co 1ML/Ni 2ML on W(110). Ni(1) and Ni(2) denote Ni in the first nearest layer and second nearest layer from W(110) substrate. From [93].

| atom          | magnetic moment [$\mu_B$] |
|---------------|---------------------------|
| Ni 1ML        | W 0.0                     |
|               | Ni 0.0                    |
| Ni 2ML        | W 0.0                     |
|               | Ni(1) 0.0                 |
|               | Ni(2) 0.0                 |
| Co 1ML/Ni 2ML | W 0.0                     |
|               | Ni(1) 0.1                 |
|               | Ni(2) 0.6                 |
|               | Co 2.0                    |

axis of easy magnetization of the surface ferromagnetic atoms does not exist for Ni 1ML and 2ML on W(110). In Fig. 21, we show the LDOS of Ni atom in Ni(111) surface (Fig. 21(a)) and Ni 1ML on W(110) (Fig. 21(b)). In the interface between Ni 1ML and W(110) substrate, 0.4 electrons transfer from a W atom to a Ni atom. This result shows that the unoccupied minority spin states in Fig. 21(a) are occupied by electrons from W atom and the LDOS change to Fig. 21(b). Therefore, Ni 1ML on W(110) lose magnetic moment.

For a Co 1ML/Ni 2ML on W(110), we obtain that the MAE=\[E[110]-E[111]=-22\text{meV}\] \(E[111]\) denotes the energy, when all spin in the system are fixed to the [111] direction and so on. This result shows that the axis of easy magnetization axis is the in-plane direction in Co 1ML/Ni 2ML on W(110). This result agrees with the experimental observation.

The origin of magnetic anisotropy is usually ascribed to spin-orbital interaction and dipole-dipole interaction. Using the magnetic moment which is calculated using first principles calculation, we found that the dipole-dipole interaction is less than 10 \(\mu\text{eV}\). This value is much smaller than the MAE from first principles calculation. Therefore, we concluded that spin-orbital interaction is dominant over dipole-dipole interaction.

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