THE sp HYBRID BONDING OF C, N AND O TO THE fcc(001) SURFACE OF NICKEL AND RHODIUM

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This brief review focuses on the nature, kinetics, dynamics and consequences of the sp-orbital hybrid bonding of C, N and O to the Ni/Rh(001) surfaces which give rise to the same kind of “radial and then the p4g clock” reconstruction. It is identified that the “radial” and the subsequent “clock” reconstruction result from the adsorbate-substrate bond formation with sp-orbital hybridization, and that the driving force behind the reconstruction originates from the electrostatic interaction along the \( h_{11} \) direction. At the initial stage, \( A^{-1} \) (\( A = C, N \) or \( O \) adsorbate) sinks into the fourfold hollow site and forms one bond with a \( B \) (\( B = Ni \) or \( Rh \) host atom) underneath, giving rise to an \( AB_5 \) cluster with four dipoles at the surface. As \( A^{-1} \) evolves into the hybridized-\( A^{-n} \) (\( n = 4, 3, 2 \)), the \( AB_5 \) cluster evolves into an \( AB_4 \) tetrahedron. Meanwhile, the \( AB_4 \) tetrahedron redefines three of the four surface dipoles as \( B^+, B^{2+}, B^{+/dipole} \) or \( B^{dipole} \), depending on the valence value of the adsorbate. The electrostatic force arises upon repopulating the valence electrons, which creates rhombus strings along the \( h_{11} \) direction.

With the presence of nonbonding lone pairs, the clock rotation on Ni(001)-(2\( \times \)2)p4g-2N\(^{-2} \) and Rh(001)-(2\( \times \)2)p4g-2O\(^{-2} \) surfaces is initiated by the alternate attraction and repulsion in the \( h_{11} \) direction and the rotation is stabilized by bond tension; whereas the clock rotation on the Ni(001)-(2\( \times \)2)p4g-2C\(^{-4} \) surface is driven by the nonequivalent electrostatic repulsion in the \( h_{11} \) direction and the rotation is balanced by strong bond compression. The findings so far have led to technical innovation for the adhesion between diamond and metals by designing a gradient TiCN transition layer to neutralize the bond stress.

1. Introduction

The adsorption of electronegative elements such as C, N and O onto metal surfaces forms the basic processes of catalytic reaction, and hence it has attracted tremendous efforts from both theoreticians and experimentalists for several decades. The electronegative elements C, N and O play important roles in fields varying from bioelectronics, pharmacology, microelectronics, photovoltaics, mechatronics and magnetoelectronics to environmental chemistry and agricultural science. Adsorption of atomic or molecule species on surfaces modifies their electronic and atomic structural properties and hence the catalytic properties. For example, catalytic reaction with rhodium (Rh) and platinum (Pt) can promote the reaction of \( 2(CO + NO) \rightarrow 2CO_2 + N_2 \), which eliminates the two poisonous gases CO and NO from the exhaust of combustion engines for environmental protection. N and O play an important role in biosignal transformation in DNA and protein processing as well as pharmaceutical technology. Therefore, a comprehensive understanding of the bonding processes in the catalytic reaction and their consequences for the behavior of atoms and valence electrons at the surface is very important both scientifically and technologically.

Comprehensive information about the electronic process of reaction can only so far be gained by integrating observations by means of crystallography, microscopy, photoelectron spectroscopy (PES) and thermal desorption spectroscopy (TDS) with an appropriate modeling analysis. In the current presentation, a review is given of the recent advance

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in understanding the representative prototypes of catalytic reaction with the involvement of C, N and O. It has been clear that the (001) surfaces of nickel and rhodium display a similar radial and clock reconstruction when C-Ni, N-Ni or O–Rh bonds form at the surfaces. The subtle features of these systems have been intensively investigated by many advanced means. This involves techniques such as LEED, SEXAFS, photoelectron diffraction, low energy alkali ion scattering and recoil spectroscopy, photoemission spectroscopy and the STM observations as well as the first principles calculations with density functional approaches. Progress has so far been quite encouraging and there are some outstanding aspects that are very challenging for further efforts. First, a summary of the experimental observations and the existing rigid sphere models for the p4g clock reconstruction will be given in this article. Then, derivatives based on the tetrahedron bond configuration are described, which gives information such as formulae for reaction dynamics and identification of the surface atomic states. The driving forces and the bond stress are estimated based on the bond-forming premise. Next, an example of direct application of the developed knowledge is provided. The new understanding enabled us to cope well with the longstanding problem of diamond adhesion by designing a TiCN gradient layer to neutralize the strong C–metal compressive bond stress with the slight tensile N–metal bond stress. Furthermore, factors controlling the bond forming and the possible reasons for other types of reconstructions occurring to the O–Cu(001) and O–Ni(001) surfaces as well as C/N–Rh(001) surfaces are discussed. Finally, a summary is presented indicating the essentiality of considering bond forming with electron transportation and sp-orbital hybridization in dealing with catalytic reaction and designing new functional materials.

2. Experimental Observations

2.1. Phase transition

It is very interesting that the chemisorption of C and N on Ni(001) surfaces, and O on Rh(001) surface, yields the same c(2 × 2) radial reconstruction and then the (2 × 2)p4g clock reconstruction. Adsorption of molecules A (= O, N, C) is known to dissociate and to saturate at half a monolayer. The A atom fills the next nearest neighboring (nnn) fourfold hollow site of the (001) surface of B (Ni, Rh), resulting in a c(2 × 2) unit mesh of the adsorbate atoms. The metal atoms at the surface move “radial” away from the adsorbate, as illustrated in Fig. 1. Further exposure to the adsorbate gives no increase of the coverage of adsorbate but a clockwise and counterclockwise reconstruction of the substrate — a (2 × 2)p4g rotational “clock” reconstruction follows at the same adsorbate coverage. In the second “clock” reconstruction phase, surface B atoms move around the dark site center, in other words, displacement happens in the <11> direction, as shown in Fig. 2. Thereby, the mirror plane symmetries are broken at the adsorption sites, while glide plane symmetry p4g occurs. Recent investigations suggest that the clock reconstruction does not occur to the O–Ni(001) or C/N–Rh(001) surfaces.

2.2. Surface morphology

Figures 1(a) and 1(b) show the STM images of the precursor Ni(001)-(2 × 2)-2C and the

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Fig. 1. STM images of the precursor (a) Ni(001)-c(2×2)-2C17 and (b) Rh(001)-c(2×2)-2O16 surfaces, and (c) the corresponding atomic and bond (insertion) model for the A−1 induced radial reconstruction phase. Adsorbate A sinks into the hollow site and bonds to the B atom underneath (labeled 1). The A−1 polarizes and pushes up the surface neighbors (labeled 2), leading to the AB5 cluster and the overall radial reconstruction at the surfaces.
The white rhombi are free of adsorbates. It is interesting that the “white rhombi” form chains along the \( \langle 11 \rangle \) direction. For C induced depression it was imaged \( \sim 0.3 \) Å in depth on a well-resolved Ni(1 \times 1) substrate. At large C coverage above 40 L exposure to ethylene (C\(_2\)H\(_4\)) at \( T \sim 530\)–650 K, p4g ordered structure becomes apparent. The reconstruction observed has been described as the rotation of the black squares resulting in the p4g symmetry. This distortion preserves the shape of the black squares and creates the white rhombi. It can be found that the STM images of Ni(001)-(2 \times 2)p4g-2C, Ni(001)-(2 \times 2)p4g-2N and Rh(001)-(2 \times 2)p4g-2O are substantially the same despite a slight difference in the angle of rotation. The C-induced lateral displacement of Ni was measured as 0.55 \( \pm 0.10 \), slightly greater than that determined with LEED.\(^4\) Klink et al.\(^{17}\) and Mercer et al.\(^{16}\) indicated that at the critical C coverage the surface is driven into a \((2 \times 2)p4g\) structure by a disorder–order phase transition mechanism — Ising universality. It is interesting to note that the Ni(100)-(2 \times 2)p4g-2N STM image exhibits two orientations of the depressions. With slight deviation, one is along the [10] direction and the other close to the [01] direction. These observations challenge identification of the individual atomic states of the surface Ni atoms altered during the reaction.

2.3. Atomic geometry

LEED studies\(^5\) on the O–Rh(001) surface revealed the presence of several LEED patterns that vary with oxygen exposure and reaction temperature. The SPA–LEED (spot profile analysis–LEED) studies of Baraldi et al.\(^{6}\) suggested that the phase transition in the O–Rh(001) also belongs to the Ising universality, or order–disorder transition. It is confirmed that the O–Rh(001) reaction proceeds in three outstanding stages,\(^{16,24}\) i.e. the disordered p(2 \times 2)-O, ordered c(2 \times 2)-2O radial reconstruction and ordered c(2 \times 2)p4g-2O clock reconstruction patterns. The c(2 \times 2)-2O and c(2 \times 2)p4g-2O phases require the same local oxygen coverage of 0.5 ML. There are conflicting opinions regarding the position of the oxygen adsorbate. Using the combination of LEED, low energy alkali ion scattering and recoil spectroscopy, Shen et al.\(^{13}\) determined that the oxygen is located 0.6 \( \pm 0.1 \) Å above the top Rh atomic plane compared with that (\( \sim 1.0 \) Å) in the earlier determination.
using LEED.\textsuperscript{3,5} A recent LEED profile simulation by Baraldi \textit{et al.}\textsuperscript{6} and density functional approximations by Alfe \textit{et al.}\textsuperscript{18,19} suggested that the O adsorbate is located 1.05 ± 0.05 Å above a white rhombus and has an off-centered asymmetric shift of 0.29–0.35 Å along the longer axis of the white rhombus. Therefore, it is very difficult to determine accurately the position of the light adsorbate. This uncertainty may be due to the multiple solutions in mathematical calculations.

For the C–Ni(001) and N–Ni(001) surfaces, the most complete analysis of the reconstruction was performed by Sotto \textit{et al.}\textsuperscript{25} Gauthier \textit{et al.},\textsuperscript{26} and Kilcoyne \textit{et al.}\textsuperscript{10–12} It was suggested that the reconstruction yields the lateral 0.55 ± 0.20 Å displacement of Ni atoms and the adsorbate is located 0.1 ± 0.1 Å above the fourfold hollow site. The estimated adsorbate–metal bond lengths are 1.82 to the surface four Ni atoms and 1.99 Å to the one beneath the adsorbate. The metal interlayer distances are considerably altered as compared to the bulk (1.76 Å) of a clean Ni(001) surface: an 11% expansion is found of the first metal interlayer spacing to \( d_{21} = 1.954 \) Å, while the second layer spacing is contracted by 2% to \( d_{23} = 1.726 \) Å. The layer spacing relaxation shows similarity to that induced by oxygen chemisorption. It has been clear that oxygen-induced relaxation is a consequence of oxide bond formation in which the oxygen is located at positions between the top two atomic layers. Bond geometry determines the first layer separation while the alternated states and sizes of atoms in the second layer reduced the separation between the second and the third atomic layer.

2.4. Valence density of state

Electronic structure studies\textsuperscript{27,28} of the Ni(001)-(2 \( \times \) 2)p4g-2C surface suggested that the presence of C leads to a decrease in the density of state around the Fermi energy. This effect coincides with the catalyst poisoning activity of certain electronegative elements, such as sulfur and phosphorous.\textsuperscript{29} Hayden \textit{et al.}\textsuperscript{30} identified, using a \( k \)-resolved inverse PES, that C, N and O induce features in the energy range of 1–4 eV above \( E_F \) for the precursor Ni(001)-c(2 \( \times \) 2) phases. They suggested that these features are due to 2p-related antibonding states. The adsorbate 2p-induced occupied states for all three structures are mainly in the −4 eV (C) to −6 eV (O) binding energy range. PES investigations\textsuperscript{20,21,31,32} discriminated that oxygen induces significant change in the energy states about 2–6 eV below the Fermi level. Density function studies\textsuperscript{18,19} derived two important DOS peaks occurring during the O–Rh(001) reaction. One is at \( \sim 6 \) eV below \( E_F \) and the other \( \sim 1 \) eV above \( E_F \). Figure 3 compares the ARPES spectra from the Rh(001)-c(2 \( \times \) 2)-2O and Rh(001)-(2 \( \times \) 2)p4g-2O phases obtained by Mercer \textit{et al.}\textsuperscript{31} At some azimuth angles, the density of state below \( E_F \) is emptied for both the chemisorbed phases and additional O derivatives can be identified at around \( \sim −5 \) eV for c(2 \( \times \) 2)-2O. It should be noted that the DOS feature at \( −5 \) eV lowers a little with an additional feature at about \( −2.0 \) eV at some azimuth angles for the p4g second phase. Interpretation of these PES features becomes easier now by considering the process of electron transportation.\textsuperscript{33,34} The DOS features above \( E_F \) can be attributed to the antibonding metal dipoles. The features at \( \sim 2.0 \) eV below \( E_F \) originate from the nonbonding lone pairs of the adsorbate and the DOS features farther below \( E_F \) result from the adsorbate–metal bonding. The similar DOS features for nitrogen adsorption onto the Ru(0001) surface have also been derived in density functional calculations by Schwegmann \textit{et al.}\textsuperscript{35} Four features correspond to the antibonding (\( \sim 3.0 \) eV), hole (−1.0 eV), nonbonding (−3.0 eV) and bonding (−6.0 eV) states, being quite similar to that of oxides as discussed.

2.5. Thermal desorption and bond strength

For the O–Rh(001) surface, desorption spectroscopy studies\textsuperscript{24,36–38} revealed that the O–Rh(001) reaction involves three phases corresponding to different bond strengths.\textsuperscript{39,40} The first state gave no ESD (electron-stimulated desorption) up to 350 K, when it converts to a state tentatively assigned as the “oxygen atom state.” For temperatures above 500 K a new state, assigned as the “oxide state” appears. The latter two states yield oxygen ions of different kinetic energies. As indicated by Comelli \textit{et al.},\textsuperscript{40} no clear characterization of these oxygen adsorption states has been achieved and the temperature and oxygen doses involved seem to exclude that a real oxide is involved.

Fisher and Schmiegel\textsuperscript{41} have reported three peaks (820, 920 and 1325–1200 K corresponding enthalpy
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Fig. 3. Angle-resolved photoelectron emission spectra from Rh(001) clean (broken lines), (a) (2 × 2)-2O and (b) (2 × 2)p4g-2O phases. Holes can be found from both the chemisorbed surfaces below the $E_F$ and additional O-derivatives can be identified at around $\sim 5.0$ eV for (2 × 2)-2O. The feature at $-5.0$ eV shifts to $-6.0$ eV, with an additional feature at about $-2.0$ eV at some azimuth angles. These features correspond to the bonding states and the nonbonding states respectively (see Fig. 5).

is 210, 260 and 360 KJ/mol) in the TDS spectrum of oxygen on Rh(100) due to desorption of atomically adsorbed oxygen, as well as one molecularly adsorbed state. Desorption from the >1200 K state corresponds to desorption from the p(2 × 2) structure and is second order. The 920 K state showed first order kinetics and corresponded to desorption from the c(2 × 2) phase. The 820 K peak was associated with desorption from the p4g structure. This implies that the adsorption enthalpy of oxygen in this structure is 50 kJ/mol lower. At the structural level, the formation of this structure is associated with rotation of the Rh atoms surrounding the oxygen atom and an increase of the coverage to the stoichiometric value of 0.5 ML. The desorption and photoemission spectral features of the O{Rh(001) are substantially the same as those observed from the O{Pd(110) and O{Rh(110) surfaces. Unfortunately, the TDS database for the N{Ni(001) and C{Ni(001) is not yet available. The oxygen exposure dependence of the TDS data for the O{Pd(110) has provided a dynamic picture of the oxide-bond-forming dynamics that coincides with that determined by LEED calculations for the O–Cu(001). The coincidence of the bonding dynamics of O{Pd(110) and O–Cu(001) indicates that oxygen forms bond with these two surfaces in four discrete stages. Detailed information about the bonding dynamics and its consequence on the valence DOS features will be introduced in Sec. 4.1. Information should be of help in understanding the TDS features for the O–Rh(001) reported by Fisher and Schmieg.

3. Rigid Sphere Models

3.1. Centered pyramid

The atomic disposition in the radial and clock reconstruction was first described by a rigid sphere model originated by Onuferko et al., based on LEED simulation in the late 1970’s [see Fig. 4(a)]. This model specifies that the adsorbate deposits above the nnn fourfold hollow sites. The adsorption of A
Fig. 4. Comparison of the rigid sphere models of (a) the centered pyramid proposed by Onufenko et al.\textsuperscript{33} and (b) the off-centered rhombus developed by Alfè et al.\textsuperscript{18} Model (a) represents a strain relief mechanism which specifies that the oxygen adsorbate is located above the center of the black square which rotates to release the bond compression. Model (b) stands for the oxygen adsorbate oscillating along the longer axis of the rhombi, which rotates clockwise and counter clockwise.

causes an expansion of the hollow, i.e. the four B atoms surrounding the site are displaced radially away from the adsorbate site. To facilitate this expansion, the four B atoms move tangentially and cause the adsorbate-contained (1 × 1) unit cells in alternate clockwise and counterclockwise rotations, giving rise to the p4g symmetry. During the process, the compressive bond stress is released through rotating the AB$_5$ pyramid. This model was later confirmed by the STM observations as given in Fig. 2, and the STM depressions are correlated with the adsorbate sites.

3.2. Off-centered rhombus

Besides the stress relief mechanism of Onufenko et al.\textsuperscript{3} an off-centered rhombus model [see Fig. 4(b)], has recently been proposed by Alfè et al.\textsuperscript{18,19} through density functional approximation and supported by LEED optimizations\textsuperscript{6} for the O–Rh(001) clock reconstruction. It was pointed out that a different substrate reconstruction is compatible with LEED and STM data. Density functional calculations and LEED simulation suggested that it is the white rhombus rather than the black square in the STM image to rotate be responsible for the asymmetric clock reconstruction mechanism. It was also suggested that oxygen atoms occupy two equivalent low symmetry sites separated by a low energy barrier in the middle of the rhombus. Alfè et al. explained that what is actually observed in the STM pictures and LEED optimizations is the average position of the oxygen atoms jumping back and forth between the two equilibrium positions in a rhombus, in the high temperature disordered phase. It was also suggested that oxygen atoms tend to shorten the bonds with the neighboring Rh atoms. The bond contraction deforms the adsorption site, which corresponds to the asymmetric clock reconstruction of the white rhombus. The driving force for the asymmetric reconstruction was assumed to be from the oscillation of the oxygen adsorbate in the two equivalent bonding sites in the rhombus and the process of bonding and rebonding at a very low, yet unknown critical temperature. Calculations\textsuperscript{18} indicated that the off-centered rhombus model is only suitable for the O–Rh(001) clock reconstruction but the C/N–Ni(001) clock reconstruction follows Onufenko’s bond-stress-relief mechanism.

3.3. Challenges

The difference between the centered pyramid and off-centered rhombus models lies in the oxygen location, which is extremely difficult to determine due to the assumption made in numerical calculations and the resolution of the instrument of detection. One model specified that the oxygen position corresponds to the apical site of a pyramid; the other, to the apical site of the off-centered rhombus. In both models, the oxygen adsorbate is located above the top atomic layer. Actually, oxygen in the latter model is located at an apical site of a quasi-tetrahedron if one considers the “adsorbate oscillation” effect — with slight lateral displacement in the rhombus. No doubt, the two rigid sphere models have made significant contribution to the understanding of the observations. For example, the centered pyramid explains the driving force for the reconstruction and the signatures of the STM images. The off-centered rhombus specifies that the oxygen adsorbate prefers three surface nearest atomic neighbors for a tetrahedron. However, the rigid sphere representations relate less to the electronic processes of the surface reaction, and hence the rigid sphere descriptions limit our understanding of the spectral features of TDS and PES. Actually, atomic dislocation or crystal reconstruction is just one aspect of the consequences of surface chemical bond formation. What we need to know are the individual atomic states, the driving force and the bond stress of the reconstructed systems, and finally we have to find means of controlling the process of bond making and bond breaking for technical applications.
As a complement to the above two rigid sphere models, a set of models in terms of bond making, band forming\textsuperscript{47} and potential barrier modification\textsuperscript{48} has been developed upon intensive LEED verification on the particular O–Cu(001) surface reaction.\textsuperscript{49–51} The model has been applied to the current “radial and clock” reconstruction systems.\textsuperscript{52–54} The aim of such attempts was initially to integrate the observations of not only the crystallography and microscopy but also the spectroscopy of desorption and photoelectron emission, and find the correlation between the corresponding signatures and the process of bond formation. Desorption profiles provide us with information about the activation energy of individual bond breaking,\textsuperscript{33,39} or the strength of individual bonds, and the photoelectron emission furnishes us with information about the evolution of the density of state in the valence band during the reaction. Information about bond geometry that determines atomic dislocation can be obtained roughly through LEED decoding. STM observations provide information about surface charges that determined the shape of the surface potential barrier. Integrated information may provide us with a comprehensive view on the origin and consequences of C, N and O chemisorption that may lead us to the common sense governing the interaction of the electronegative elements with metal surfaces, and eventually to technical applications.

4. Bond Formation: Dynamics and Kinetics

4.1. Chemical bond and valence band

Models in Fig. 1(c) and in the right hand column of Fig. 2 show the bond models for $A^{-1}$ and $A^{-n}$ ($n = 2, 3, 4$, respectively). The models represent briefly that the electronegative element A can react with arbitrary element B of less-electronegative to form a tetrahedron through bonding orbitals (sharing electron pairs) and nonbonding electron lone pairs. $A^{-1}$ forms first with one bond to the B atom underneath in the current specific cases and then $A^{-n}$ follows with $sp$-orbital hybridization. Then the adsorbate forms a quasi-tetrahedron with four atomic neighbors. In a tetrahedron, the number of bonding orbitals is $n$ (= valence value of A) while the number of nonbonding orbitals is “$4 - n$.” For reaction involving nitrogen and oxygen, there are one and two nonbonding lone pairs, respectively, in a tetrahedron. For carbide formation, Raman low frequency spectroscopy investigations have confirmed that no lone pair is produced.\textsuperscript{55} The $sp$ hybridization is an intrinsic feature of the $p$-shell elements and the hybridization does not happen unless the $n$ bonding orbitals of the adsorbate are fully occupied.\textsuperscript{56} The lone pair production with $sp$-orbital hybridization happens and it is independent of the other bonding component.

It should be noted that reaction is a process in which chemical bond forms with the transfer of valence electrons. Consequently, the surface atomic states change; atomic sizes and atomic positions change. Additionally, the $sp$-orbital hybridization and the lone pair production will induce dipoles of metal atoms. For carbide, nitrides and oxides, electrons transfer from the outer shell of the host materials to the empty $2p$ orbitals of the adsorbate that are far below the $E_F$. This process decreases the density of state below the $E_F$ of the host while adding features to the host in the energy range of $2p$ levels of the adsorbates. It should also be noted that the bond lengths and bond angles are retractable within a limit depending on the bonding coordination environment\textsuperscript{57,58} and such bond contraction is independent of the nature of a particular chemical bond.\textsuperscript{59} For instance,\textsuperscript{58} if the coordination reduces from 12 to 4, the ionic bond length contracts by 0–12%. Unlike oxygen and nitrogen, carbon can form bonds with $sp^2$-, $sp^3$-orbital hybridization. In principle, the $sp^2$ hybrid prefers $C_{3v}$ symmetry with three hybrid bonds to its neighbors in one plane while the $sp^3$ hybrid tends to bond to four neighbors identically. A third allotropic state of carbon, fullerenes or nanotubes has been identified but the bond nature still needs to be established. Besides the nonbonding lone pair production that is the intrinsic production of $sp$-orbital hybridization of the adsorbate, the nature of the C–Ni, N–Ni or O–Rh bond in a tetrahedron is polar-covalent because of the difference in electronegativity [$\Delta \eta = 2.5(C)/3.0(N) - 1.8$ (Ni) = 0.7/1.2; $\Delta \eta = 3.5(O) - 2.2(Rh) = 1.3$]. It was clearly indicated by Pauling\textsuperscript{60} that if $\Delta \eta$ equals or is greater than 2 the bond is ionic, and otherwise polar-covalent.

The dynamics of bond forming can be described as follows. Initially, adsorbate A sinks into the four-fold hollow site and bonds to one B atom underneath [labeled 1 in Fig. 1(c)]. Consequently, $A^{-1}$
It should be noted that in both of the A
−
A
neighbors, as shown in the insertion in Fig. 1(c). As
sent metal B
the insertions in Fig. 2. The atoms labeled 1 repre-
level of the host metal are fully occupied (for the
other. Originally, the energy states below Fermi
energy change when they transfer from one state to
Arrows represent the dynamic processes of electron
process moves electrons from below the
E
ative additives catch electrons to form the bond. This
process moves electrons from below the
E
and the bonding states. The nonbonding lone pairs induce metal dipoles with energy
higher than the
E
Because of bonding and dipole formation, holes are
produced right below the Fermi level.

When A
−
hybridization develops, an evolution of the
band configuration of the host metal occurs. In
the case of nonbonding lone pair production (n < 4),
the bonding band is divided as an
sp
-bonding sub-
band and a nonbonding (lone pair) subband. The
lone pair subband is located at a certain place be-
tween the bonding subband and the Fermi level.
For a number of oxides the lone pair states have
been identified at −1.5 eV below
E
.61–65 The lone-
pair-induced dipoles sustain the antibonding features
above the
E
in the energy band. For carbide with-
out nonbonding lone pairs, there is no subband of
nonbonding states and there are no longer antibond-
ing dipoles. The processes of bond formation and the
antibond formation create holes below the
E,
which creates a band gap
E
9 to the host metals or widens
the band gap from
E
9 to
E
1 of semiconductors. This may provide insight into the mechanism of wide
band gap compound semiconductors such as oxides and nitrides.

Upon overdosing of nitrogen or oxygen (n < 4),
hydrogen-bond-like forms. The dipoles will then con-
tribute their electrons to the bonding orbitals of ad-
tional adsorbates. The arrow from the antibond-
states to the
sp
-bonding subband represents the
process of the H-bond-like formation. Therefore, the
width of the antibonding subband decreases and
the system becomes more stable.
Compared with compounds of other electronegative elements, the energy band of carbide is modified by the processes of bond formation and hole production without nonbond and antibond features. Electrons are transported from the outer shell of Ni to the C–Ni bonding and produce holes below the Fermi level. This illustrates well, with the theoretical findings of McConvville et al. and Darling et al., that the presence of C leads to a decrease in the density of state at the surface around the Fermi energy.

On the other hand, bond formation produces A$^{-n}$, B$^+$ ions and B$^{\text{dipole}}$ at surfaces. This roughens the surface on an atomic scale. B$^+$ reduces its size considerably. For the Cu example, the atomic radius reduces from 1.28 Å to 0.53 Å when the Cu becomes Cu$^+$. With increase in the dimension, B$^{\text{dipole}}$ protrude from the surface. Therefore, it is possible to specify an individual atomic state at the surface with the aid of STM imaging.

### 4.2. Reaction dynamics

The dynamic processes of B(001)–c(2 × 2)-2A$^{-1}$ and B(001)–(2 × 2)pp4g-2A$^{-n}$ can be expressed as follows [see the corresponding 2 × 2 unit cell in Figs. 1(c) and 2]:

\[
A_2(\text{adsorbate}) + 4B(\text{surface}) + 4B(2\text{nd layer}) \\
\Rightarrow 2A^{-1}(\text{subsurface}) + 2B^+(\text{2nd layer}) \\
+ 2B(2\text{nd layer}) + 4B^{\text{dipole}} (A^{-1}-\text{induced})
\]

and then, for \( n = 2 \) (oxygen),

\[
\Rightarrow 2A^{-2}(\text{hybrid}) + 2B^{\text{dipole}} (\text{surface}) \\
+ 2B^{+/\text{dipole}}(\text{surface}) + 2B^+(\text{2nd layer}) \\
+ 2B(2\text{nd layer}),
\]

for \( n = 3 \) (nitrogen),

\[
\Rightarrow 2A^{-3}(\text{hybrid}) + 2B^+ (\text{surface}) \\
+ 2B^{+/\text{dipole}}(\text{surface}) + 2B^+(\text{2nd layer}) \\
+ 2B(2\text{nd layer}),
\]

for \( n = 4 \),

\[
\Rightarrow 2A^{-4}(\text{hybrid}) + 2B^+ (\text{surface}) \\
+ 2B^2+(\text{surface}) + 2B^+(\text{2nd layer}) \\
+ 2B(2\text{nd layer}).
\]

During the reaction, an AB$_5$ cluster evolves into an AB$_4$ tetrahedron. In the c(2 × 2)-2A$^{-1}$ phase, A sinks into the hollow site and bonds to the B atom underneath. The A$^{-1}$ polarizes and pushes the electron cloud of the surface atoms radially away from the central adsorbate. In the second phase, the c(2 × 2) cell reforms into two rhombi (without adsorbate) and two squares with adsorbate inside, as can be seen from Fig. 2, leading to the overall clock and counter-clock reconstruction. The A$^{-n}$-hybrid requires four neighbors for the tetrahedron. As the A$^{-n}$ has already bonded to one B underneath, the tetrahedron, for the O–Rh example, defines one B$^+$ (labeled 1) and two lone-pair-induced B$^{\text{dipole}}$ (labeled 2) of the four nearest surface neighbors. As can be seen from the primary unit cell containing the adsorbate, three of the four surface neighbors are labeled 1 or 2. As the surface atomic ratio A : B = 1 : 2, half of the entire B(001)–(2 × 2)pp4g-2A$^{-n}$ surface atoms are defined as B$^{\text{dipole}}$ (or B$^+$) and the other half as B$^{+/\text{dipole}}$ (or B$^{2+}$), as compared in Table 1.

It is noted that the unlabeled B atom in Fig. 2 changes its position in a clockwise way if one traces the adsorbate along the (11) direction. It is also seen along the (11) direction that the unit cells without adsorbate form chains of rhombi with alternation of orientations. This leads to the rhombi chain as highlighted in the STM images and in the corresponding structural models. From the symmetric point of view, it would be essential to consider a c(4√2 × 4√2)-16A$^{-n}$ complex unit cell according to the periodicity requirement of label 1 in Fig. 2 for the currently clock-reconstructed systems.

### 4.3. Rhombi chain and surface atomic states

The STM images in Fig. 2 display two distinct features. First, a rhombi chain bond network covers the overall reconstructed surface. Second, the shape and orientations of the STM depressions in N–Ni(001) differ from those of C–Ni(0010) and O–Rh(001) surfaces.

Figure 6 shows a single rhombi chain extracted from the three reconstructed surfaces. The rhombi chain is composed of B atoms labeled “2–2–1–1–2–2”. For C–Ni(001), label 1 is Ni$^+$ and label 2 is Ni$^{2+}$. For N–Ni(001), label 1 represents Ni$^+$ and label 2 the Ni$^{+/\text{dipole}}$. For O–Rh(001), label 1 stands for Rh$^{\text{dipole}}$ and label 2 for Rh$^{+/\text{dipole}}$. Apparently, the electrostatic charges of 1 and 2 are not equal for all the cases. For the N and O chemisorbed system, the intensity of interaction along the rhombi chain is in such an order: 2–2 ~ 1–1 > 0 > 1–2 < 0, because the B$^{+/\text{dipole}}$ is slightly positive compared to
Effective charge factor $\varepsilon = 0.5(1 + \Delta \eta/2)$ is taken into account in calculating the driving force. According to Pauling, if $\Delta \eta \geq 2$ the bond is ideally ionic.

<table>
<thead>
<tr>
<th>$(2 \times 2)p4g$</th>
<th>O/Rh(001)</th>
<th>N/Ni(001)</th>
<th>C/Ni(001)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic radius (Å)</td>
<td>O: 0.74/0.66</td>
<td>N: 0.88/0.70</td>
<td>C: 0.914/0.771</td>
</tr>
<tr>
<td>(CN = 12/1)</td>
<td>Rh: 1.342/1.252</td>
<td>Ni: 1.244/1.149</td>
<td></td>
</tr>
<tr>
<td>Electronegativity</td>
<td>3.5/2.2</td>
<td>3.0/1.8</td>
<td>2.5/1.8</td>
</tr>
<tr>
<td>$\varepsilon = \varepsilon_c + \Delta \eta(\varepsilon_i - \varepsilon_c)/2$</td>
<td>0.825</td>
<td>0.80</td>
<td>0.675</td>
</tr>
<tr>
<td>Goldschmidt ionic radii (Å)</td>
<td>O$^{2-}$: 1.32</td>
<td>N$^{-3}$: 1.71</td>
<td>C$^{-4}$: 2.60</td>
</tr>
<tr>
<td>Pauling ionic radii (Å)</td>
<td>O$^{2-}$: 1.76</td>
<td>N$^{-3}$: 2.47</td>
<td>C$^{-4}$: 4.14</td>
</tr>
<tr>
<td>Rotation angles $\Phi$ (°)</td>
<td>0.0; 9.0</td>
<td>0.0; 12.0</td>
<td>0.0; 20.0</td>
</tr>
<tr>
<td>Electrostatic forces $F_i$</td>
<td>7.99; 11.09</td>
<td>8.21; 14.59</td>
<td>−3.11; −91.17</td>
</tr>
<tr>
<td>Bond stress $F_b$ (dyne)</td>
<td>$-F_i$</td>
<td>$-F_i$</td>
<td>$-6.22; 89.66$</td>
</tr>
<tr>
<td>Tangent shift $S$ (Å)</td>
<td>0.30</td>
<td>0.37</td>
<td>0.64</td>
</tr>
<tr>
<td>Bond expansion $\Delta L/L$ (%)</td>
<td>1.2</td>
<td>2.2</td>
<td>6.4</td>
</tr>
<tr>
<td>Intensity of interaction</td>
<td>2-2 $\approx$ 1-1 $&gt; 0 &gt;$ 1-1 $\approx$ 2-2 $&gt; 0 &gt;$ 2-2 $&gt; 2$-1 $&gt; 1$-1</td>
<td></td>
<td></td>
</tr>
<tr>
<td>along the rhombus chain</td>
<td>2-1</td>
<td>1-2</td>
<td>$&gt; 0$</td>
</tr>
<tr>
<td>Surface atomic states</td>
<td>1: dipole</td>
<td>2: +/dipole</td>
<td>1: +</td>
</tr>
<tr>
<td>2: +/dipole</td>
<td>1: +</td>
<td>2: +</td>
<td></td>
</tr>
<tr>
<td>Driving forces for rotation</td>
<td>$\pm F_i; F_b$</td>
<td>$\pm F_i; F_b$</td>
<td>$F_b; \pm F_i$</td>
</tr>
</tbody>
</table>

Fig. 6. The rhombus-chain extracted from the STM images from which one can estimate the electrostatic force driving the clock and counterclockwise rotation of the adsorbate-contained $(1 \times 1)$ unit cells.

the B$^{\text{dipole}}$ and it is slightly negative with respect to B$^{+}$. The repulsion of 2-2 and 1-1 and the slight attraction between 2 and 1 displace the B atoms, and consequently the overall clock reconstruction. Therefore, for the system with N/O, the electrostatic force drives the clock reconstruction. On the other hand, 2-1 will come closer without otherwise a bond tension to balance the electrostatic force. So the balance of the bond tension against the electrostatic force stabilizes the clock rotation of the surface atoms. However, for the C-contained system the intensity of interaction is 2-2 > 1-2 > 1-1 > 0. Namely, the electrostatic repulsive force dominates throughout the rhombi chain. A response of force to balance the overall repulsion is necessary. Therefore, the final equilibrium reconstruction is a resultant of the electro repulsion and a response of bond compression.

It is surprising that though the crystallography and the STM images appeared quite similar, the driving force and the bond stress are entirely different for systems with chemisorbed nitrogen/oxygen and carbon.

It is to be noted that from the rhombi chain point of view, the p4g STM image is substantially the same despite the rotation angles. However, from the shape of the depressions the nitride image differs much from that of both the C-Ni(001) and O–Rh(001). The Ni(001)-(2 $\times$ 2)p4g-N STM image shows two orientations of the alternative thick lines of depressions. With slight deviation, one orientation is along the [10] direction and the other close to the [01] direction. Linking the Ni$^{+}$ ions labeled 1 in N–Ni(001) (see Fig. 2), one can find that the 1-1 bridge matches ideally the orientations of the STM depressions. This verifies that the radius of the Ni$^{+}$ ion is much smaller than that of Ni$^{+}$/dipole. Therefore, the individual atomic states of the surface Ni atoms can be identified by applying the model of bond formation to the STM images.
4.4. Atomic dislocation and surface relaxation

Measuring the sharp angle $\Theta$ of a rhombus in the STM images, one can estimate the lateral displacements of the B atoms, as derived in Fig. 7. The sharp angle of the rhombus measured from Fig. 2 are $\Theta = 50^\circ$(C–Ni), $66^\circ$(N–Ni) and $72^\circ$(O–Rh). The adsorbate-contained unit cell then rotates $\Theta = (90^\circ - \Theta)/2 = 20^\circ$, $12^\circ$ and $9^\circ$, which displaces the B atom along the $\langle 11 \rangle$ direction, $S = \sqrt{2}r \times tg \Phi$, where $r$ is the atomic radii of Ni(1.244 Å) or Rh(1.342 Å). The rotation of a primary $(1 \times 1)$ unit cell expands the dimension ($L$) by about $\Delta L/L = 1/\cos \Phi - 1 = 6.4\%$, 2.2\% and 1.2\%, for C, N and O chemisorption, respectively.

It can be easily understood that the first layer spacing expands depending on the bond geometry as the adsorbate is located between the top two atomic layers. The second layer spacing contraction is due to the fact that the B$^+$ forms in the second layer. The reduction in atomic size and the stronger interaction between the B$^+$ ions and the B third atomic layer should be responsible for the second layer spacing contraction. Unfortunately, rigid sphere models with adsorbate resting above the top plane could not explain the surface relaxation, as it seems unlikely that the light adsorbate could “pull out” the entire top atomic layer without external forces acting on the adsorbates.

4.5. Driving forces and bond stress

Without knowing the exact dipole moment, we may assume a Coulomb interaction between the atoms forming the rhombi chain. Because of the valence charge screening effect, the net charge transfer between the adsorbate and B atoms can be estimated by introducing an effective charge factor: $\varepsilon = \varepsilon_c + \Delta \eta (\varepsilon_i - \varepsilon_c)/2$; $\varepsilon_c = 0.5(\Delta \eta = 0)$ and $\varepsilon_i = 1.0(\Delta \eta = 2)$ correspond to covalent and ionic states, respectively. For the O–Rh example, $\Delta \eta = 3.5 - 2.2 = 1.3$, $\varepsilon = 0.825$. The chain contains an infinite number of atoms ($n = \pm 100$ is sufficient for estimation). It is easy to find out the Coulomb potential $V_i$ and the corresponding electrostatic force $F_i$ acting on the $i$th atom in the rhombi chain:

(a) Induced by nitrogen and oxygen adsorption:

$$V_i = \frac{1}{4\pi \varepsilon_0} \sum_{j \neq i} \frac{q_j}{r_{ij}} = \frac{\varepsilon}{4\pi \varepsilon_0} \sum (-1)^j \left[ \frac{1}{(2j-1)a - 2s} - \frac{1}{(2j-1)a + 2s} \right].$$

(b) Induced by carbon adsorption:

$$V_i = \frac{1}{4\pi \varepsilon_0} \sum_{j \neq i} \frac{q_j}{r_{ij}} = \frac{\varepsilon e}{4\pi \varepsilon_0} \left\{ \frac{2}{a - 2s} + \frac{1}{a + 2s} \right\} + \sum_{j=1} \left[ \frac{1}{2} \frac{1}{(4j-1)a + 2s} + \frac{1}{(4j + 1)a - 2s} \right].$$

and

$$V_{i+1} = \frac{1}{4\pi \varepsilon_0} \sum_{j \neq i+1} \frac{q_j}{r_{ij}} = \frac{\varepsilon e}{4\pi \varepsilon_0} \left\{ \frac{1}{a - 2s} + \frac{2}{a + 2s} \right\} + \sum_{j=1} \left[ \frac{2}{(4j - 1)a - 2s} + \frac{1}{(4j + 1)a - 2s} \right].$$

The electrostatic force along the $\langle 11 \rangle$ direction:

$$F_i = -q_i \frac{dV_i}{dr_{ij}}.$$ 

The corresponding response of bond stress is

$$F_b = \frac{F_i}{\sqrt{2 \{1 + \cos[2(90^\circ - \Phi)]\}}}.$$
Figure 7 compares the \( \Phi \) dependence of the electrostatic forces \( F_i \) induced by the chemical adsorption of electronegative elements of C, N and O.

Table 1 summarizes the kinetics and dynamics of these systems. For the N–Ni(001) example, when the tetrahedron rotates from 0 to 12°, \( S \) shifts from 0 to 0.37 Å. The electronic force \( F_i \) increases from 8 to 15 dyne. A corresponding bond tension, \( T_b \) is \( \sim 36 \) dyne. The driving force \( F_i \) is balanced at 12° by the bond tension \( T_b \). Obviously, if \( \Phi > 12° \), the bond tension is greater than the \( F_i \); otherwise, the bond tension is smaller than the \( F_i \). The \( F_i \) for N–Ni and O–Rh is somewhat overestimated, because dipole interaction takes the \( r_{ij}^{-6} \) form other than simply the Coulomb potential. However, this can be precisely quantified, provided with a known dipole moment. For C–Ni(001), the intensity of the interaction \( F_i, F_{i+1} \) on the Ni\(^{2+}\) and Ni\(^{2+}\) and the bond stress can also be estimated. When \( \Phi \) rotates from 0 to 20°, the electronic force \( F_i \) acting on atom \( i \) (Ni\(^{2+}\)) increases from \(-3\) to \(-91 \) dyne; for Ni\(^{2+}\) the force \( (F_{i+1}) \) changes from \(-6\) to \(+90 \) dyne. As can be seen from Fig. 7, initially, both the Ni\(^{2+}\) and the Ni\(^{2+}\) tend to move away from the center of 2-2 due to the stronger repulsion between Ni\(^{2+}\)–Ni\(^{2+}\), compared to the repulsion between Ni\(^{2+}\)–Ni\(^{2+}\). At a certain angle (\( \sim 4° \)) the force \( F_{i+1} \) acting on Ni\(^{2+}\) changes its direction and reaches 90 dyne at 20°. Obviously, repulsion between Ni\(^{2+}\) and Ni\(^{2+}\) supplies compression \( (F_b) \) to the C–Ni bond, which stabilizes the system. The bond compression \( F_b \) is estimated \( \sim 133 \) dyne.

Unfortunately, no advanced database is available yet for comparing the bond stress. However, the model enables us to justify that the driving force for the C/N–Ni(001) and the O–Rh(001) clock reconstruction comes from the interaction between localized charges along the \( (11) \) directions and further rotation of the tetrahedron is constrained by the bond compression for C–Ni or bond tension for N–Ni and O–Rh.

5. Comparison with Other Reconstructed Surfaces

We have so far gained some new understanding about the typical clock reconstruction of the fcc(001) surface induced by C, N and O. However, questions may arise:

(i) Why does oxygen derive different reconstruction patterns to the fcc(001) of Rh and Cu?
(ii) Why does the same kind of clock reconstruction not happen to O–Ni(001) or C/N–Rh(001)?

First, we may look at the factors determining the bond formation, and as a consequence the surface reconstruction. Such factors have been identified as: (i) the difference in electronegativity, (ii) the geometrical orientation and (iii) the scale of the lattice constant of the host. It does not matter what the nature of the host element is.

Cu(001) and Rh(001) surfaces share the same fcc(001) geometry, but the electronegativity and lattice constant are different. It has been confirmed that, on the O–Cu(001), oxygen forms pairing CuO\(_2\) pyramid and then the Cu\(_3\)O\(_2\) pairing tetrahedron.\(^{56}\) Obviously, the difference in reconstruction pattern between O–Rh(001) and O–Cu(001) comes from nothing more than the minor difference in their atomic radii \((1.342 – 1.277 = 0.065 \) Å\) and electronegativity \((2.2 – 1.9 = 0.3)\). For the Cu(001), the smaller hollow \(|d = 2R(\sqrt{2} – 1) = 1.058 \) Å\) and the lower electronegativity \((1.9)\) cause the O \((d = 1.32 \) Å\) to bond one surface atom first, and then to another one underneath. For the Rh(001), the greater hollow \((1.112 \) Å\) and the higher electronegativity \((2.2)\) enable the O to sink into the hollow site; yielding a Rh\(_3\)O cluster. For the O–Cu(001), evolution of the off-centered pyramid to the pairing tetrahedron gives first the nanometric Cu(001)-\((2 \times 2)\) domains\(^{67}\) with protruding boundaries and then the missing-row-type Cu(001)-(\(\sqrt{2} \times 2\sqrt{2}\))R45° reconstruction,\(^{68-70}\) or the Cu\(_3\)O\(_2\) pairing tetrahedron. For the O–Rh(001), interaction among the localized charges produces the “rhombi chain” that rotates the tetrahedron, leading to the overall p4g reconstruction. Although the reconstruction patterns and the corresponding observations are not the same, the basic element of \( sp \)-orbital hybridization of oxygen and the production of nonbonding states are the same in the two cases. The O\(^{−1}\) formation and the O\(^{−2}\) tetrahedron bond formation provide the basic building element for oxidation happening to transition metals such as Cu\{001\}, \((110),^{71,72}\) \((111)^{73}\) and noble metals such as Rh\{001\}, \((110),^{74}\) \((111)^{75}\) as well as Ru(0001)\(^{76}\) and Co(10\(\bar{1}\)0)\(^{77}\) the analogs to fcc(110) and fcc(111), as we have recently described\(^{78-81}\) consistently with the developed
knowledge. No matter how complicated the reconstruction is shown to be, the basic tetrahedron bond configuration and the electronic process of oxidation are the same. Consequently, the oxygen-derived DOS features in the valence band of metals are the same despite the complexity of the crystal geometry and surface morphology of various metals.

Ni(001) and Rh(001) surfaces share the same fcc crystal geometry but their lattice constants and the values of electronegativity are different, as compared in Table 1. Similarly, the greater difference in electronegativity between oxygen and Ni (3.5–1.8 = 1.7) enables oxygen to bond to the Ni atom more easily than to the Rh atom. Therefore, oxygen bonds to the Ni atom in the top plane, giving rise to no “clock” reconstruction.\(^{82}\) Although the radii of C and N are slightly greater than that of oxygen, the smaller difference in electronegativity between C/N and Ni (2.5/3.0 – 1.8 = 0.7/1.2) allows the C/N adsorbate to be located at the fourfold hollow site before the adsorbate can catch electrons from the B atom underneath. The very small electronegativity difference between C/N and Rh (2.5/3.0 – 2.2 = 0.3/0.8) should be the reason why the C and N cannot form the clock reconstruction on the Rh(001) surface though the atomic radii of C and N are slightly larger than that of oxygen.\(^{18}\)

6. Technical Application: Diamond Adhesion

Here we show an example for technological applications of the improved knowledge. Based on the knowledge and further experimental verifications about the surface bond stress induced by C, N and O reaction to Ti and tungsten carbide surface, we have designed a TiCN gradient transition layer that joins the synthetic diamond to the metal substrate seamlessly.

Synthetic diamond films can be obtained by chemical vapor deposition (CVD) in which a mixture of H\(_2\) and CH\(_4\) is used as the medium of fabrication. Hydrogen plasma etches the weakly bonded carbon and carbon radicals derived from the ionization of CH\(_4\) during the process of diamond deposition. The adhesion of diamond films to metal substrates has been a critical and long-standing issue that prevents the practical application of the excellent properties of synthetic diamond. The poor adhesion of diamond to metals has been attributed to the mismatch of thermal expansion,\(^{83}\) and graphitization\(^{84}\) by the penetration of ferromagnetic elements such as Co, Ni and Fe during the deposition of diamond thin films at elevated temperature.\(^{85}\) The adhesion of diamond to metals could be improved by introducing a buffer layer of Cr nitride,\(^{84}\) engineered Ti nitride,\(^{86}\) TiC and TiCN,\(^{85}\) SiC,\(^{87}\) or by Ti ion implantation.\(^{88}\) The laser-engineered TiN buffer layer could enhance the mechanical interlock strength of the diamond/metal system due to the increased contacting areas between the diamond and the substrate.\(^{86}\) However, the mechanism of applying the buffer layers is not yet clear and such implementation should be conducted based on design, which requires better understanding of the interaction of hydrogen, carbon and nitrogen with metals.

Results in Table 1 indicate that the surface charge states and the bond stress of these reconstructed surfaces are different though the Ni and Rh may not represent essentially various metals. However, it should be noted that although the surface morphology and crystallography vary from case to case and from material to material in the chemisorbed systems, the valence values of the atoms surrounding the electronegative additives should be certain. This means that as a consequence of sp-orbital hybridization, oxygen forms a tetrahedron with four arbitrary atoms through two sharing electron pairs and two nonbonding electron lone pairs, which produces two metal “+” ions and two lone-pair-induced metal dipoles. Interaction of the metal dipoles with oxygen and hence with the bulk metal is as weak as the van der Waals bond because there is no charge transfer between oxygen and the dipoles. Because of the strong repulsion between the electron lone pairs, metal dipoles tend to be located at the open end of a surface. Generally, the oxide surface is composed of the weakly bonded metal dipoles. Similarly, the sp-orbital hybridization enables a nitrogen adsorbate to generate three metal “+” ions and one metal dipole while carbon produces four metal “+” ions at the apices of a tetrahedron. As compared in Table 1, the C–Ni(001) surface is fully covered by Ni\(^+\) and Ni\(^{+2}\) and the estimated bond compressive stress (–139 dyne/bond) at the equilibrium state is much higher than the tensile stress for N–Ni and O–Rh. The N–Ni(001) surface is covered by Ni\(^+\) and Ni\(^{+2}/\)dipole with bond tension of ~36 dyne. The O–Rh(001) surface is
composed of Rh\textsubscript{h} dipole and Rh\textsuperscript{+}/dipole with a bond tension of \(\sim 35\) dyne. The metal “+/dipole” plays dual roles as lone-pair-induced dipole and as “+” to provide electron to the adsorbate. The current analysis and further experiments\textsuperscript{89} examining C, N and O plasma sputtering effect on nucleation and adhesion of diamond on Ti substrate revealed that:

(i) It is the weakly bonded dipoles and the negative surface charges of oxide that prevent the nucleation and growth of diamond on an oxide precursor. Raman spectroscopy revealed the presence of oxide characteristics in low frequency vibrations after O plasma sputtering.

(ii) The strong bond compression and the positive surface charges of carbide determine the poor adhesion of diamond to metals. Thicker (< 10 \(\mu\)m) diamond films peeled off the substrate indicating compressive bond stress.

(iii) The weak bond tension and the nearly neutral surface charges of nitride may be beneficial to the diamond adhesion. However, a thicker nitride layer accumulates the tensile stress, showing cracks that also affects the adhesion.

The analytical and experimental results have therefore prompted us to design a graded Ti carbonitride interlayer. It is found to be practical to add a graded TiC\textsubscript{x}N\textsubscript{y} buffer layer before diamond deposition. The adlayer transits metal to Ti carbonitride with an increase in the carbon composition and then transists it to diamond. This layer has the function of neutralizing the bond stress as nitride suffers slight tensile stress while carbide suffers strong compressive stress. In the initial stage of diamond deposition, we may vary the concentration of C and N in the reaction gases to minimize the bond stress. Figure 8 compares the diamond thin films grown on the titanium substrate with and without the graded buffer layer. It can be seen that the porous TiC prevents adhesion while the TiCN buffer layers can combine the diamond seamlessly with the substrate. Hence, fundamental understanding of the effect of C, N and O bonding with Ni/Rh(001) metals has led to a new and practical way to solve the critical and long-lasting issue of diamond adhesion. The development of the gradient TiCN buffer layer may provide a prototype for joining non-metals to metals with good adhesion in composite materials.
7. Summary

The advance in understanding C, N and O interaction with the low index (100) surface of Ni and Rh may be summarized as follows:

- The C/N–Ni(001) and O–Rh(001) surface reaction is a dynamic process in which C$^{-1}$, N$^{-1}$ or O$^{-1}$ forms first and then C$^{-4}$, N$^{-3}$ or O$^{-2}$ with $sp$-orbital hybridization follows. The adsorbate sinks into the fourfold hollow site and forms an AB$_5$ cluster. The B atoms underneath the adsorbate become B$^+$. The full surface layer is composed of the A$^{-1}$-induced B dipoles. With the development of adsorbate hybridization, the AB$_5$ cluster evolves into an AB$_4$ tetrahedron that yields the rhombi chain network at the surface.

- The clock reconstruction is driven by the electrostatic force along the (11) direction, arising due to charge transportation. During the bond formation, the surface charge is redistributed, leading to the one-dimensional nonuniformity charge strings along the (11) directions. The electric interaction along the rhombi chain provides tangential force driving the clock rotation and the corresponding bond tension or compression that stabilizes the clock rotation. The O–Rh and N–Ni bond suffers slight tension while the C–Ni bond suffers strong compression.

- The first interlayer relaxation is determined by the bond geometry while the second layer contraction is caused by the strong interaction of B$^+$ in the second layer with the metallic third layer.

- The O–Rh(001) surface is covered with B$^+$/dipole and B$^{dipole}$ that are weakly bonded to the oxygen and hence the bulk. The N–Ni(001) surface is composed of B$^+$ and B$^+$/dipole while the C–Ni(001) consists of B$^+$ and B$_2^+$ with high compression of the bond. Therefore, the surface atomic states, the surface stress and the mechanism for reconstruction are different though the morphology and crystallography are nearly the same for the p4g- reconstructed systems.

- Understanding has so far led to the development of a gradient TiCN transition layer that joins the synthetic diamond films to the metal substrate seamlessly. The gradient Ti carbonitride interlayer neutralizes the bond stress and hence improves the adhesion between nonmetals and metals. This application may provide direct and convincing evidence for the advantages of approaches in terms of bond formation in chemisorption studies.

- Therefore, it is suggested that it is essential to consider the $sp$-orbital hybridization of the light adsorbate in dealing with catalytic reactions and designing new functional compounds.

References