Surface-structure dependent reaction of hydrogen-assisted reduction at O/Ni(110) surfaces studied by MIES and LEED*

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I. INTRODUCTION

Adsorption of atoms and molecules, and chemical reactions, such as oxidation or reduction, at Ni surfaces have been an important subject of study for a long time. This is recently prompted by the reason that knowledges about the surface preparation and the interface-formation process are necessary when one wants to apply magnetic nano-structures at these surfaces to some nano-devices. The Ni(110) surface, particularly, attracts considerable attention, because it provides many reconstruction phases depending on the adsorbed element and its coverage which may serve the study on the structure-dependency of those reactions.

The co-adsorption of oxygen and hydrogen and the oxidation/reduction reaction at Ni surfaces have been investigated with various techniques. Lescop, et al. showed that oxygen atoms are removed from a H/O(200 L)/Ni(111) surface in forms of water molecules, by MIES and UPS [1, 2]. A TPD and XPS investigation by Vesselli, et al. demonstrated that oxygen is hardly removed by hydrogen at a H(10 L)/O(~20 L)/Ni(110) surface at low temperatures (~100 K) [3]. Experiments studying a relation between the progress of surface oxidation/reduction and the atomic and electronic structure of reconstructed substrates have not been reported yet.

In the present study, we treat adsorption of hydrogen on oxygen pre-adsorbed Ni(110) surfaces and intend to construct a picture of the hydrogen-assisted reduction process being consistent with observed changes in both the substrate structure and the surface electronic states. We applied metastable-induced electron spectroscopy (MIES) to the analysis of hydrogen adsorption induced changes in the local electronic states of the O/Ni(110) surface. We will show that a reversible reaction of oxidation/reduction proceeds at surfaces covered with low densities of the Ni-O-Ni row but does not at surfaces with its higher densities.

II. EXPERIMENTAL

The apparatus is composed of a He* source, a hemispherical energy analyzer (VG Scientific) and a low-energy electron diffraction (LEED) optics. The base pressure was around 1.0 × 10^-8 Pa. A beam of helium metastable atoms was produced by high-voltage discharge at a nozzle-skimmer space. The main ingredient of the beam is He* 2S (excitation energy=19.8 eV), which was confirmed by a Stern-Gerlach analysis. The sample is a single-crystal Ni(110) surface, cleaned by repeated cycles of Ar+ ion sputtering and annealing. Its clean surface exhibited a clear (1 × 1) LEED pattern. The surface was exposed to oxygen and hydrogen molecular gas at room temperature.

At Ni(110) surfaces, whether clean or adsorbed with oxygen or hydrogen, He* atoms undergo resonance ionization followed by Auger neutralization owning to high work functions of those surfaces [4–6]. The electron excitation in this Auger neutralization process takes place nearly in the topmost layers, and the resultant emission spectrum reflects a self-convolution of local DOS of the
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oxygen exposures around
and its density increases up to two thirds a monolayer at
a proposed model, Ni-O-Ni atomic rows stretching along
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position for calibrating the electron energies of the MIES
high-energy cutoff due to a contribution of UV photons
target surface. Each spectrum showed a supplementary
hydrogen exposure for various O/Ni(110) surfaces.

FIG. 1: A diagram of LEED patterns as a function of the
hydrogen exposure for various O/Ni(110) surfaces.

III. RESULTS AND DISCUSSION

In our previous report [7], we showed variations in the
atomic and electronic structures in the oxidation process
of the Ni(110) surface in the range of oxygen exposure
$S_{ox}$ below 5 L using MIES and LEED. The structures of
this Ni(110) surface are classified into the following four
different types depending on $S_{ox}$: (a) At $S_{ox} = 0$ L, non-
reconstructed (1 × 1) surface; (b) at $S_{ox} \sim 0.5$ L, low
oxygen-coverage (3 × 1) surface; (c) at 1 ≤ $S_{ox}$ ≤ 3 L,
moderate oxygen-coverage (2 × 1) surface; (d) at 4 L ≤
$S_{ox}$: high oxygen-coverage (3 × 1) surface. According to
a proposed model, Ni-O-Ni atomic rows stretching along
the [001] direction on the surface plane have been created,
and its density increases up to two thirds a monolayer at
oxygen exposures around $S_{ox} \sim 5$ L.

At first we observed hydrogen-induced structural
targets for each of the above mentioned types of the
Ni(110) surface by LEED. Figure 1 shows a diagram of
LEED patterns as a function of the hydrogen exposure
for four different surfaces. When we exposed the Ni(110)
clean surface to hydrogen molecular gas, a (1 × 1) pattern
did not change even at exposures around 100 L. Although
there are some references reporting a reconstruction to the
(1 × 2) structure by hydrogen adsorption [8–10], we did
not observe such a reconstruction in LEED. At the surface
(b), the (3 × 1) structure was changed to the (1 × 1)
through the streaky (1 × 1) with increasing the hydrogen
exposure. Also the surface (c) was reconstructed to
(1 × 1) through a streaky structure by hydrogen adsorption.
However, the high oxygen-coverage (3 × 1) surface
was not led to reconstruction even by heavier hydrogen
exposures.

After the hydrogenated (1 × 1) structure was formed by
molecular hydrogen exposure of 100 L at the surfaces of
type (b) or (c), the surface was exposed to oxygen again
in order to check the reversibility of the whole reactions.
The LEED showed that an oxygen exposure of 0.5 L leads
to a (3 × 1) reconstruction and an exposure of 1 L to a (2 ×
1) structure. This observation suggests that the surface
follows a reversible path in the hydrogenation of oxidized
surfaces and the oxidation of hydrogenated surfaces.

Before the MIES experiment on the oxygen reduction,
we performed hydrogenation of the clean Ni(110) surface.
Figure 2 shows variations in the MIES spectrum taken
from the Ni(110) surface with increasing the hydrogen exposure up to
~100 L. (a) clean Ni(110), (b-i) H$_2$-exposed Ni(110) surfaces.

FIG. 2: Variations in the MIES spectrum taken from the
Ni(110) surface with increasing the hydrogen exposure up to
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hydrogen adsorption. If adsorbates induce dipole moments quite locally, the potential barrier height should increase in proportion as the adsorption proceeds. This is, however, not the case here. At a clean surface, the density distribution of mobile electrons tends to be smoothed, which effectively reduces the work function. We suppose a redistribution of those electrons at the Ni(110) surface takes place at a certain coverage with hydrogen. Then the smoothing effect will be suppressed, and the work function will be increased. The total emission intensity in the MIES spectrum was decreased at the same H$_2$-exposure range as the work-function was increased. This result supports the above consideration, because a decrease in the transition probability of Auger neutralization at the surface [7] is well explained by a disappearance of delocalized states from which an electron tunnels to the He-1s state.

Figure 3 shows a series of MIES spectra taken from the O/Ni(110)-0.5 L surface (type (b)) in the progress of hydrogen adsorption. The spectrum (b), from a hydrogen-free O/Ni(110) surface, contains a strong peak, labeled $P$$_{ox}$, at about 10.5 eV. Peak $P$$_d$, on the other hand, is weakened by the oxidation. This has been attributed to a decrease in the probability of Auger neutralization transition connecting the Ni 3d-states by an influence of oxygen adsorption [7]. When this surface was exposed to hydrogen gas for exposures of ~25 L, the intensity of peak $P$$_d$ was recovered rapidly (spectrum (d)). This suggests that the oxygen reduction proceeds and the surface restores 3d-electronic states due to bare Ni atoms. A similar effect has been found in the hydrogen-assisted reduction of the O/Ni(111) surface by Lescop, et al [1, 2].

Figure 4 shows a series of MIES spectra which demonstrates variations in the electronic structure of the O/Ni(110)-1 L surface (type (c)) by hydrogen adsorption.

The spectral variation in this case was similar to that for the O/Ni(110)-low-coverage (3×1) surface (type (b)). It is confirmed by these spectra that the reaction of oxygen reduction takes place also on such a surface with moderate coverages of oxygen. However, the reduction rate was found to be lower than the case of the type (b) surface. This is shown by the two facts: At first, the recovery of the intensity of $P$$_d$ at the (2×1) surface (type (c)) needs more amount of hydrogen exposure than for the type (b); Secondly, in the LEED observation, the appearance of the hydrogen-induced streaky (1×1) structure at the type (c) surface needs again more amount of hydrogen exposure. These results may tempt us to lead a model in which the reduction rate depends on the Ni-O-Ni row density on the O/Ni(110) surface. As the shape of MIES spectra (e-f) in Fig. 3 and (e-f) in Fig. 4 substantially agrees with the spectra for the hydrogenated surfaces (Fig. 2), one can judge that oxygen reduction of these surfaces was completed by hydrogen exposures of 50~100 L.

MIES spectra taken from hydrogen-adsorbed O/Ni(110)-4 L surfaces (type (d)) were shown in Fig. 5. Some influences of hydrogen exposure appeared: a slight decrease in the intensity of O-2p induced states, a gradual increase in the work function, and an appearance of a weak shoulder at energies corresponding to $P$$_h$. However, the overall shape of the MIES spectrum was not changed even by heavier hydrogen exposures. As already mentioned, we confirmed by LEED that the (3×1) periodicity in the structure of the type (d) surface was not changed by the hydrogen exposure. Obviously hydrogen does not effectively work in reducing the O/Ni(110)-high-coverage (3×1) surface.

We discuss possible processes of the oxida-
FIG. 5: A series of MIES spectra taken from O/Ni(110)-4 L surfaces: (a) clean Ni(110); (b) O/Ni(110)-4 L; (c-f) H$_2$-exposed O/Ni(110) surfaces.

The reaction/reduction reaction at the Ni(110) surface being based on the two principal findings of the present experiment: (i) the reduction proceeds at the low-coverage (3 × 1) surface and the (2 × 1) surface, but does not at the high-coverage (3 × 1) surface; (ii) reduction of oxidized surfaces and oxidation of hydrogenated surfaces are the reversible reaction of each other. From the result (i), a mechanism of direct attack of hydrogen molecules to adsorbed-oxygen sites is ruled out. The finding (i) means that the dissociation of hydrogen molecules needs bare-Ni 3d electronic states. The high-coverage (3 × 1) surface contains Ni-O-Ni rows so densely that it may be hard for incident hydrogens to directly meet the Ni-3d orbitals. Since the Ni-O-Ni bonds are much stronger than the Ni-H-Ni bonds [3], one cannot explain the reversibility of the reaction (the result (ii)) only from the viewpoint of energetics. This problem can be tricked by assuming a fast step of production of intermediate compounds. In this case H$_2$O may be a proper candidate, and actually Vesselli, et al. detected such species in their TPD spectra.

IV. CONCLUSION

We applied MIES and LEED to the study of hydrogenation of the O/Ni(110) surface. The reaction of hydrogen-induced reduction took place at both the low-coverage (3 × 1) surface and the (2 × 1) surface, but did not at the high-coverage (3 × 1) surface. The reaction rate of oxygen reduction strongly depends on the surface structure, that is, on the density of Ni-O-Ni rows in the present case, which is consistent with the model of dissociation of hydrogen molecules at surface sites with the bare-Ni 3d electronic states. The reactions, reduction of oxidized surfaces and oxidation of hydrogenated surfaces, was shown to proceed reversibly. These results suggest an intermediate product, such as water molecules, which needs further experiments by other techniques.

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