Analysis of positron annihilation spectra and reemitted positrons from clean and hydrogen adsorbed Ni(111) surfaces

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Abstract. The positron annihilation γ-ray spectra emitted from clean and hydrogen adsorbed Ni(111) surfaces are measured. We have discussed the disordered structures of adsorbed-hydrogens on Ni(111) surface studied by the positron annihilation spectra and reemitted slow positrons. The present experiments suggest the presence of the positronium hydride, PsH, on hydrogen-saturatedly adsorbed Ni(111) surface.

1. Introduction

The adsorption mechanism of hydrogens on transition-metal surfaces has been investigated extensively, because it is very important to application such as catalytic reaction. Especially the H/Ni(111) system is a typical example. Its phase diagram of adsorbed hydrogens for the order-disorder transition has been obtained by Christmann et al. [1] from the temperature variation of the low-energy electron diffraction (LEED) half-order spot intensity. The hydrogen atoms occupy threefold sites of a hexagonal (so-called honeycomb) structure, and the saturation coverage is around \( \theta = 1 \) monolayer [1]. 2×2-H phase contains 2H atoms per unit cell and this corresponds to a coverage of \( \theta = 0.5 \). The order-disorder transition temperature is highest for the structure with \( \theta = 0.5 \), and strongly decreases with disorder being introduced. This phase diagram clearly reveals an asymmetry with respect to \( \theta = 0.5 \). It is much wider on the low coverage side than on the high coverage one, which can be explained by the amount of disorder introduced by more vacancies and interstitial H atoms. The disordered structure on the high-coverage side is not known. On the hydrogen-chemisorbed Ni(111) surface, two temperature-programmed-desorption (TPD) peaks, \( \beta_1 \) and \( \beta_2 \), have been observed [1]. The structure, which corresponds to the \( \beta_2 \) state of the hydrogens on Ni(111) surface is (2×2)-2H superstructure. On the other hand, the structure of the disordered state of adsorbed hydrogens of the \( \beta_1 \) state is not yet known. Reemitted slow-positron spectroscopy [2] will provide important information on adsorbed light atoms on surfaces. In this study, we have measured the changes in positron annihilation spectra and reemitted slow-positrons from hydrogen-adsorbed Ni(111) surface due to different adsorbing conditions of hydrogens on Ni(111) surface. The origin of the changes in reemitted slow positrons due to different adsorbing conditions will be discussed.
2. Experiment

The positron beam intensity is ~3000 counts/s. We installed the LEED and Auger electron spectroscopy (AES) optics in the experimental chamber. The mesh of the ground level is installed in front of the sample. By changing the sample bias, information for the energy spectra of positive particles emitted from a surface of the sample can be obtained. When 35.0 V is imposed on the sample, positive particles from the surface are accelerated in the direction of the channeltron. Three meshes are installed in front of the channeltron. By changing the voltage of the center mesh and fixing the ground level on other two meshes, information for the energy distribution of positive particles can be obtained. When -20 V is imposed on the sample, a small number of positive particles (about 3 counts/600 s) are emitted from the sample. This means that the measured counts contain ~3% as reflected positrons and relatively highly energetic hydrogen ions (above 20 V). From the previous study [3], it is known that the ratio of positive ions to positrons is very low. So it is thought that most positive particles in the present study correspond to positrons. Positron annihilation spectra are measured with high-purity germanium detector. The sample is suspended by W wires and can be annealed by direct current through the wires. The highly pure hydrogen and argon gases can be introduced to the UHV chamber through a variable leak valve. The base pressure of the UHV chamber was 2.6×10^-10 Torr. The specimen surface is cleaned by repeated argon ion bombardment. No contamination was checked by the Auger electron spectra. Then cleaned Ni(111) surface was annealed for 30 min at 1100 K to eliminate defects in 2.0×10^-9 Torr. After the sample cools to room temperature, a sharp (1×1) LEED pattern was observed. After the sample was cooled by liquid nitrogen and then hydrogen gas at some conditions was introduced at 220 K, typical (2×2)-2H LEED pattern was observed. Reemitted slow positrons from hydrogen-adsorbed Ni(111) surface are measured in some adsorbing conditions. Furthermore, the Doppler broadening spectra of the positron annihilation from hydrogen-lightly adsorbed Ni(111) surface and hydrogen-saturatedly adsorbed one are measured.

3. Results and Discussion

On all low-index Ni surface, H adsorbs dissociatively. The Ni(111) surface remains unreconstructed under H exposure. Hydrogen seems to absorb in the hollow site [1], and the saturation coverage is θ ~ 1 monolayer. The hydrogen coverage is estimated qualitatively from hydrogen exposure (1 L = 1.0×10^-6 Torr×1 s) and LEED patterns. At a coverage θ = 0.5, the Ni(111) surface exhibits a well-defined (2×2)-2H superstructure. However, adsorbed hydrogens in the saturation coverage have the disordered structure, which is not yet known. Here, we can observe only diffraction spots of Ni(111) surface structure. We cannot observe diffraction spots of adsorbed hydrogens due to the disorder structure. The number of thermalized positrons that diffuse back to the surface is given by

$$L = \int_{0}^{\infty} P(z)N(z)dz,$$

where $P(z)$ is a positron stopping profile in the case of incident energy of 1.97 keV in Ni, and $z$ is the distance from the surface. $N(z)$ is the total flux through the plane of the surface due to the initial δ-function profile at $z$, and is represented as

$$N(z) = \exp\left[-\frac{z}{\sqrt{(D_{\tau_{\text{eff}}})^2}}\right] \frac{1}{1 + \beta/(D_{\tau_{\text{eff}}})^2},$$

where $D_{\tau_{\text{eff}}}$ are the positron diffusion constant ~0.7 cm²/s [4] and the positron-annihilation lifetime ~100 ps [5] in Ni, respectively. $\beta$ is a coefficient that takes account of internal reflection at the surface. Since the positron work function is ~1.3 eV in Ni [6], thermalized positrons which diffuse back to the surface are emitted from the surface to vacuum as reemitted slow positrons. Oishi et al. [7] have observed that the number of reemitted slow positrons from hydrogen-saturatedly adsorbed Ni(111) surface is reduced much in comparison with that from the clean Ni(111) surface. Recently we
have measured reemitted slow positron yields from hydrogen-adsorbed Ni(111) surface on different adsorbing conditions [8]. Work function of Ni(111) surface and positron-annihilation lifetime are changed by hydrogen adsorption on Ni(111) surface. Figure 1 shows normalized counts/20 min of reemitted slow positrons from hydrogen-adsorbed Ni(111) on hydrogen-introduction conditions. It is seen that the reemitted slow positron yield is maximum in the (2×2)-2H superstructure on Ni(111) surface. It is suggested strongly that increase of the reemitted slow positron yield in the (2×2)-2H superstructure is related to increase of the electron work function due to the hydrogen adsorption. An interesting experimental result is that the electron work function changes remarkably owing to chemisorption of hydrogen on the Ni(111) surface. The electron work function increases linearly by 165 meV up to \( \theta \sim 0.5 \) followed by a slight decrease as the \( \beta_1 \) chemisorption state is filled [1]. And the collision with highly dense adsorbed hydrogens induce more trapping of reemitted slow positron on hydrogen saturatedly adsorbed Ni(111) surface.

![Figure 1](image.png)

Figure 1. Normalized counts/20 min of reemitted slow positrons from hydrogen-adsorbed Ni(111) on hydrogen-introduction conditions.

Figure 2 shows the total counts of the Doppler broadening spectra of the positron annihilation \( \gamma \)-ray emitted from the hydrogen adsorbed Ni(111) surface in some adsorbed conditions (from clean Ni(111) surface to hydrogen-saturatedly adsorbed one). This result is consistent with reduction of reemitted slow positrons from the hydrogen-saturatedly adsorbed Ni(111) surface [7]. Since the escaping of reemitted slow positrons and ortho-positroniums from hydrogen-saturatedly adsorbed Ni(111) surface is less than that of hydrogen-lightly adsorbed one, the total count of the Doppler broadening spectrum emitted from hydrogen-saturatedly adsorbed Ni(111) surface increases in comparison with that from hydrogen-lightly adsorbed one. It is seen that the Doppler broadening spectra counts is not minimum in the (2×2)-2H superstructure on Ni(111) surface. Figure 3 shows S-parameter of the Doppler broadening spectra of the positron annihilation \( \gamma \)-ray emitted from the hydrogen adsorbed Ni(111) surface in some adsorbed conditions (from clean Ni(111) surface to hydrogen-saturatedly adsorbed one). It is of significance that the S-parameter of the positron annihilation spectrum of hydrogen-lightly adsorbed Ni(111) surface is higher than that of hydrogen-saturatedly adsorbed Ni(111) surface. This result suggests that relative contribution of para-positronium in the spectrum seems to increase on the hydrogen-lightly adsorbed Ni(111) surface, because escaping of the ortho-positronium from the hydrogen-lightly adsorbed Ni(111) surface increases in comparison with that from the hydrogen-saturatedly one. The total counts and S-parameter of Doppler broadening spectra (the positron-annihilation spectra) seem not to show the maximum or minimum at the coverage of \( \sim 0.5 \) ML. This might be due to that the Doppler broadening spectra contain many effects such as annihilation of para-positroniums, pick-off annihilation of ortho-positroniums, and positron annihilation in the near-surface. These experimental results show that three-annihilation \( \gamma \)-rays from ortho-positronium around the hydrogen-lightly adsorbed Ni(111) surface are reduced in comparison with those around the hydrogen-saturatedly adsorbed Ni(111). Now we might be able to explain the origin of the reduction of the reemitted slow-positron by adsorbed hydrogen atoms in
saturated coverage as follows, that is, the interaction between highly dense adsorbed hydrogen atoms and reemitted slow-positron might disturb strongly emission of thermalized slow positrons into vacuum, and as a result positron annihilation of two $\gamma$-rays emitted from the surface increases. Furthermore the collision between highly dense adsorbed hydrogen atoms and ortho-positroniums might induce more trapping of ortho-positroniums on hydrogen-saturatedly adsorbed Ni(111) surface. Trapping of ortho-positroniums might suggest the presence of positronium hydride, PsH, on hydrogen-saturatedly adsorbed Ni(111) surface. The positronium hydride, PsH, has been observed in hydrogen-adsorbed graphite-alkali metal intercalation compounds [9].

4. Conclusion
We have measured reemitted slow-positron yields from hydrogen-adsorbed Ni(111) surface on different adsorbing conditions. It is seen that the reemitted slow-positron yield is maximum in the (2×2)-2H superstructure on Ni(111) surface. It is suggested strongly that increase of the reemitted slow-positron yield in the (2×2)-2H superstructure is related to increase of the electron work function due to the hydrogen adsorption. And we have measured the positron annihilation $\gamma$-ray spectra from hydrogen-adsorbed Ni(111) surface on different adsorbing conditions. It is suggested that the collision with highly dense adsorbed hydrogens induces more trapping of reemitted slow positrons and ortho-positroniums on hydrogen saturatedly adsorbed Ni(111) surface. This might suggest the presence of...
the adhesive state of ortho-positroniums, such as the positronium hydride, PsH, in adsorbed hydrogens on hydrogen-saturatedly adsorbed Ni(111) surface.

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