Positron annihilation study of the disordered phase of hydrogen adsorbed on the Ni (111) surface

S Komagata1, F Hori1, A Iwase1, H Suzuki2, K Hirota2, I Kanazawa2, K Fukutani3, K Nozawa4 and F Komori4
1Department of Materials Science, Osaka Prefecture University, 1-1 Gakuen-cho, Naka-ku, Sakai, Osaka 599-8531, Japan
2Department of Physics, Tokyo Gakugei University, 4-1-1, Koganei-shi, Tokyo 184-8501, Japan
3Institute of Industrial Science, University of Tokyo, 4-6-1, Meguro-ku, Tokyo 153-8505, Japan
4Institute of solid state Physics, University of Tokyo, 5-1-5, Kashiwa-shi, Chiba 277-8581, Japan
E-mail: komagata-s@mtr.osakafu-u.ac.jp

Abstract. The adsorption of hydrogen on transition-metal surface has been studied by both experimental and theoretical methods. Hydrogen adsorbed Ni (111) surface had measured by using slow positron beam apparatus. The positron annihilation γ-ray energy spectra emitted from hydrogen-adsorbed Ni (111) surfaces are analyzed. We have discussed the stability of the disordered phase of adsorbed hydros on Ni (111) surfaces. Positron annihilation results showed that the disordered phase is unstable until about 300K.

1. Introduction
The motivation to investigate hydrogen-surface interaction phenomena arises from various viewpoints. First, we have to mention the field of heterogenous catalysis in which a great part of the reactions involve hydrogen as a reactant or product molecule. On the hydrogen-chemisorbed Ni(111) surface, two temperature-programmed desorption (TPD) peaks, β₁ and β₂, have been observed [1]. The structure, which corresponds to the β₂ state of the hydros on Ni (111) surface, is (2×2)-2H superstructure. On the other hand, the structure of the disordered state of adsorbed hydros of the β₁ state is not yet known.

Reemitted slow-positron spectroscopy [2] will provide important informations on adsorbed light atoms on surfaces. In this study, we have measured the changes in positron annihilation spectra from hydrogen-adsorbed Ni (111) surface due to different adsorbing conditions of hydros on Ni (111) surface. Oishi et al. [3] 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 [4]. In this study, we have analyzed the positron annihilation spectra from the disorder state of adsorbed hydrogen, and discuss the stability of the disordered state. Especially, it is shown that the disorder state is unstable about ~300K.
2. Experiment
The slow positron beam is composed of two stages. The first stage positron-beam system is composed of a $^{22}\text{Na}$ positron source ($\sim 3\text{mCi}$) and a W single crystal (100) foil of 1 m thickness. The W foil has been annealed in an Ultra High Vacuum (UHV) chamber at $\sim 2300\text{K}$, is attached 5mm apart from the isotope for moderating positrons. The slow positrons are extracted from the moderator using an accelerating grid of 15V, and are guided along the magnetic field through the solenoid tube of the first stage. The extracted slow positron beam is guided in vacuum along a magnetic field toward the measurement chamber. The field ($60 \sim 80 \text{ Gauss}$) is supplied by solenoid coils directly wound around the vacuum transport tube, and is supplemented with Helmholtz coils at several positions where the chamber of the $^{22}\text{Na}$ source cannot be backed for making UHV. Thus, we set an Al block with a cylindrical hole for differential pumping, whose diameter is 10mm and length is 40mm, at the end of the first stage. The slow positrons are transpoted through the hole and are injected into the UHV experimental chamber. When the gate valve between the Al cylinder and the transport tube is opened, the pressure of the UHV chamber increases to $4.0 \times 10^{-10}\text{Torr}$ from $2.0 \times 10^{-10}\text{Torr}$.

For the slow-positron spectroscopy, it is necessary to transfer the beam from the magnetic field of the transport system to a magnetic field-free region in the measurement chamber. To extract the beam into the magnetic field free space without changing the beam size, an electrostatic accelerator is used in the magnetic field. Without acceleration, the radius of the cyclotron motion becomes larger as the magnetic line of force expands at the end of the magnetic transport tube. The extracted positron beam is further transported to the measurement chamber by electrostatic Einzel lenses. A simulation of the trajectories of the positrons has been performed. Finally the positron beams with a diameter of a few mm and an energy of 2 keV are transported to the center of the measurement chamber for the spectroscopy. The intensity of the slow positron beam thus obtained is approximately $0.6 \times 10^4 \text{cps}$.

We installed the LEED and AGE optics in the experimental chamber. Positron annihilation spectra are measured with a 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 $2.6 \times 10^{-10}\text{Torr}$. 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 1100K to eliminate defects in $2.0 \times 10^{-9}\text{Torr}$. After the sample cools to room temperature, a sharp $(1 \times 1)$ LEED pattern was observed. The sample was cooled by liquid nitrogen and then hydrogen gas at some conditions was introduced at 180K. When hydrogen gas $1.0 \times 10^{-8}\text{Torr}$ is introduced in the chamber for 5min at 180K, typical $(2 \times 2)\text{-H}$ LEED pattern was observed. The positron annihilation $\gamma$-ray energy spectra from hydrogen-saturated adsorbed Ni(111) are measured at 180K to 350K.

3. Results and Discussions
The order-disorder problem of a honeycomb lattice such as H/Ni(111) has been considered theoretically [5, 6]. Nagai et al [7] have discussed the order-disorder transition in H/Ni(111) on the basis of position-space renormalization-group (RG) calculations. They considered the following inter particle (hydrogen) interactions; (A) nearest-neighbor exclusion, second-neighbor repulsion, and third-neighbor attraction, which was previously proposed by Domany et al [8], (B) nearest-neighbor exclusion, second-and third-neighbor repulsions, and further-neighbor interactions up to the sixth-neighbor one. When the interaction parameters involve are suitably adjusted, both the interaction (A) and (B) lead to the phase diagrams in good agreement with the experiment by Christmann et al. [1] In both theoretical and experimental phase diagrams [1, 7], there in only one phase of disorder (liquid) in hydrogen-coverage region $\theta > 0.6$. Oishi et al. [3] have observed that the reemitted slow positron yield is reduced in the disordered phase on hydrogen-saturatedly adsorbed Ni(111). Origin of the reduction of reemitted slow positron yield in the disorder phase is not confirmed. It is expected theoretically that charge flows from the surface to wards the hydrogen addatom, causing a dipole moment and, in turn, an electrostatic
repulsion between the hydrogen addatoms [9]. That is, in high coverage case, the repulsion between the adsorbed hydrogen atoms remarkably. In addition, the repulsion is strongest for those hydrogen atoms that are located in a large distance away from the surface, because the surface electrons cannot screen the repulsion interaction among these hydrogen atoms.

Recently we have observed that counts of the annihilation spectra around 511keV emitted from hydrogen-saturately adsorbed Ni (111) increase in comparison with those from hydrogen-lightly adsorbed Ni (111) [10]. This is coexistent with reduction of reemitted slow positrons from hydrogen saturatedly adsorbed Ni (111). It is seen that the value of s-parameter decreases remarkably on the hydrogen saturatedly adsorbed Ni (111) surface [11]. 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-ray 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-saturately adsorbed Ni (111) surface. Fig.1 shows counts of the positron annihilation spectrum around 511keV emitted from hydrogen-adsorbed Ni(111) surface at each temperature. Counts at 180K and 300K are attributed to the positron annihilation γ-ray spectra emitted from Ni(111) surface of the hydrogen exposure ~80L (1L=1.0×10^{-6}×1s). As shown Fig.2 the value of s-parameter increases. In this condition (saturately hydrogen-adsorbed surface), (1×1) LEED pattern was observed at 180K as shown in Figure 3 (a). This shows the disorder phase of adsorbed hydrgens. As shown in Fig.1 when temperature from 300K to 350K, counts of the positron annihilation γ-ray spectrum decrease remarkably. Also (1×1) LEED pattern was observed at 350K. Subsequently when this sample is kept on hydrogen exposure at 180K, (2×2)-2H LEED pattern appears as shown in Fig.3 (b). The results show that the disorder phase of adsorbed hydrgens is unstable above ~300K and the hydrogen gas phase might exist above ~300K. That is, if the phase above ~300K is hydrogen-gas state, the interaction between adsorbed hydrgens and reemitted slow-positrons decreases in comparison with one of hydrogen-saturately adsorbed state (the disorder phase). Thus reemitted slow positron yield increases and, as a result, the counts of the positron annihilation γ-ray spectrum emitted from the surface decreases at 350K, furthermore, the collision between adsorbed hydrgens and ortho-positroniums is reduced at 350K, and, as a result, more ortho-positroniums are emitted from the surface to vacuum. Thus the value of s-parameter increases, and the three-annihilation rate from the surface decreases, when temperature increases from ~300K to 350K. 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-saturately one [10]. The present results suggested strongly that there is a boundary line between the disorder phase and the gas phase in the phase diagram.

Figure 1. Counts of the positron annihilation spectrum around 511keV emitted from

Figure 2. S-parameter of the Doppler broadening spectra of the positron annihilation
hydrogen-adsorbed Ni (111) surface at each temperature.

- ray emitted from the hydrogen adsorbed Ni (111) surface at each temperature.

Figure 3 (a). LEED pattern of 1×1 (hydrogen-saturate) at 180K.

Figure 3 (b). LEED pattern of (2×2)-2H at 180K when after heat.

4. Conclusion
We have discussed the stability of the disorder phase of adsorbed hydrogens on Ni(111) surface, analyzing the positron annihilation γ-ray spectra emitted from the surface. It is suggested that there is a boundary line between the disorder phase and the gas phase in the high H-coverage region in the phase diagram.

5. References
[1] K Christmann, R J Behm, G Ertl, M A V Hove, and W H Weinberg 1979 J. Chem Phys. 70 4168
[2] I Kanazawa, T Wada, Y Oishi, Y Terashima, K Fukutani, Y Murata, Y Ito, K Nozawa, F Komori 2005 Nucl. Instrum. Methods Phys. Res. B 232 299
[3] Y Oishi, T Wada, I Kanazawa, K Fukutani, Y Murate, Y Ito, K Nozawa, K Komori 2005 Appl. Surf. Sci. 241 119
[4] S Komagata, K Hirota, H Suzuki, M Osawa, S Arii, I Kanazawa, K Fukutani, K Nozawa and F Komori 2008 Appl. Surf. Sci. 255 227
[5] E Domany and M Schick 1979 Phys. Rev. B 20 3828
[6] R C Kittler and K H Bennemann 1979 Solid state Common. 32 403
[7] K Nagai, Y Ohno, T Nakamura 1984 Phys. Rev. B 30 1461
[8] E Domany, M Schick and J S Walker 1979 Solid State Common. 30 331
[9] G Kresse and J Hafner 2000 Surf. Sci. 459 287
[10] S Komagata, H Suzuki, K Hirota, I Kanazawa, K Fukutani, K Nozawa and F Komori 2010 J. Phys. 225 012029
[11] S Komagata, K Hirota, S Arii, I Kanazawa, K Fukutani, K Nozawa, F Komori 2008 Surf. Inter. Anal. 40 1713