

Behaviour of adsorbed hydrogen on Ni(111) surface and reemitted slow positron

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We have performed the measurement of reemitted slow-positron spectroscopy for the clean Ni(111) surface and hydrogen adsorbed Ni(111) surface. It is suggested strongly that the disordered hydrogen-adsorbed structure of the β_1 state contains many vacancy-like defects. It is reported that increase of the reemitted slow positron yield in the (2×2) -2H superstructure on Ni(111), in comparison with that from clean Ni(111) surface, is much related to increase of the electron work function due to the hydrogen adsorption.

Key words: Adsorbed hydrogen, Ni(111) surface, reemitted slow positrons

1. INTRODUCTION

The determination of the property of atomic species with solid surfaces has recently attracted considerable interest. Particularly the interaction of hydrogen with nickel surfaces represents one of the most extensively investigated subjects in surface science [1-3]. This is partly due to the catalytic properties of this metal in hydrogenation reactions. In addition, hydrogen adsorption on solid surfaces is the initial step for a variety of surface and bulk phenomena such as hydrogen storage in materials and hydrogenation reactions.

On Ni(111) surface, hydrogen is believed to be adsorbed in the hollow site, and the saturation coverage is around $\theta = 1$ monolayer. At a coverage of $\theta = 0.5$, the surface structure exhibits a well-defined (2×2) -2H superstructure [1,4], which corresponds to the higher binding state β_2 in two bindings β_1 and β_2 of thermal desorption spectra [1,3].

In addition, the interesting experimental result is that the electron work function changes remarkably due to the chemisorption of hydrogen on Ni(111) surface. An almost linear increase of the electron work function up to approximately 165 meV at $\theta \sim 0.5$ is followed by a slow decrease as the β_1 chemisorption state is filled [1]. Upon a further increase from $\theta \sim 0.5$, intensity of the $(1/2, 1/2)$ fractional-order beam decreases and approaches zero at $\theta \sim 0.75$, because fraction of the disordered structure of the β_1 state increases [1]. The disordered structure of the β_1 state is not known.

Recent studies with positron-annihilation-induced Auger electron spectroscopy (PAES) [5], reflection high-energy positron diffraction (RHEPD) [6,7], and positron-induced ion desorption [8,9] demonstrate that the low-energy positron is a strongly sensitive probe for detecting adsorbed atoms on the surface. In addition, it has been expected that reemitted slow positron spectroscopy will provide important information for adsorbed light atoms and vacancy-type defects near the

surface.

In this study, we have performed the measurements of reemitted slow positrons from the clean Ni(111) surface and hydrogen-adsorbed Ni(111) surface, and report the change in reemitted slow positron yield due to increase of the electron work function due to the hydrogen-adsorbing. It has been suggested that the disordered structure of the β_1 state contains many positron-trapping sites such as vacancy-like defects.

2. Reemitted slow-positron spectroscopy

The slow positron beam for reemitted slow positron spectroscopy is composed of two stages [8,9]. The first stage positron-beam system is composed of a ²²Na positron source (~ 3 mCi) and a W single crystal (100) foil of $1 \mu\text{m}$ thickness, which has been annealed in an UHV chamber at $\sim 2300\text{K}$, is attached 5 mm apart from the isotope for moderating positrons. The slow positrons are extracted from the moderator using an accelerating grid of 15 V, 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 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 ²²Na source cannot be backed for making UHV. Thus, we set an Al block with a cylindrical hole for differential pumping, whose diameter is 10 mm and length is 40 mm, at the end of the first stage. The slow positrons are transported 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 4.0×10^{-10} Torr from 2.0×10^{-10} Torr.

For the reemitted 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 [10]. Finally the positron beams with a diameter of a few mm and an energy of 2 to 4 keV are transported to the center of the measurement chamber for the spectroscopy. The intensity of the slow positron beam thus obtained is approximately 0.6×10^4 cps.

Fig.1 shows the schematic diagram of the target optics geometry for reemitted slow positron spectroscopy. The mesh of the ground level is installed in front of the sample with the face of mesh and the surface of the sample set toward the channeltron. By changing the sample bias, information can be obtained on the energy of the positive particles. When 10V is imposed on the sample, positive particles at the surface are accelerated in the direction of the channeltron.

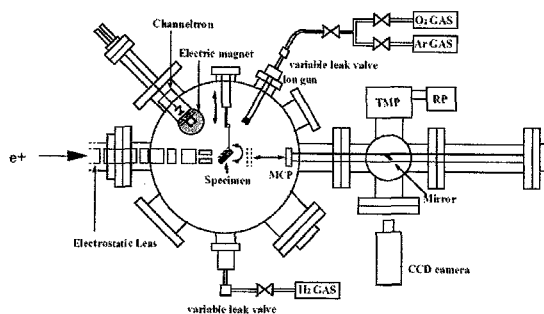


Fig.1 Apparatus of the target-optics geometry for reemitted slow-positron spectroscopy.

Three meshes are installed in front of the channeltron. By changing the center mesh voltage, information can be obtained on the energy distribution of positive particles passing through the mesh. A permalloy sheet is installed between the magnet and the electrostatic lenses in the measurement chamber so that the magnetic field gives no effect on the incident positron beam. The sample is suspended by W wires, and can be annealed by direct current through the wires. The highly pure hydrogen and argon gas can be introduced to the UHV chamber through variable leak valve. The specimen surface is cleaned by repeated argon ion bombardment and annealing to 1000K. Finally, the clean Ni(111) surface was annealed for 30min at $\sim 1000\text{K}$ to eliminate defects in 6.0×10^{-10} Torr. After the Ni crystal cools to room temperature, hydrogen gas at 1.0×10^{-8} Torr is introduced in the chamber for 5min through a trap at liquid nitrogen temperature for the adsorption of hydrogen atoms on the clean Ni(111) surface.

3. Results and discussion

On Ni surface, there is a covalent interaction of the H_2 molecular bonding and antibonding states with local density of state of the surface. The covalent bond between the H_2 states and 3d states of Ni create new molecule-metal bonding and antibonding levels.

If the d-band is close to the Fermi level, the new H_2 -3d antibonding state will be above the Fermi level, i.e. unoccupied, and there will be no repulsion between the molecule and the metal [11].

The number of thermalized positrons that diffuse back to the surface is given by

$$L = \int_0^{\infty} P(z)N(z)dz. \quad (1)$$

Where $P(z)$ is a positron stopping profile in the case of incident energy of 1.99keV in Ni, and z is distance from

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

D_+ and τ_{eff} are the positron diffusion constant approximately $0.7\text{cm}^2/\text{sec}$ [12] and the positron annihilation lifetime which is in the 100psec [13] in Ni, respectively.

β is a coefficient that take account of internal reflection at surface. Since the work function is about -1.3eV in Ni [14], for the positrons diffuse back to the surface, positrons are emitted from the surface to vacuum as reemitted slow positrons.

Fig.2 shows the total counts of reemitted positrons from the clean Ni surface and hydrogen saturated Ni surface as a function of the mesh voltage installed in front of the channeltron at 180K. The number of the detected reemitted positrons from the clean Ni surface is larger than that from the hydrogen saturated Ni surface, whose surface structure is an disordered one of the β_1 state. As the mesh voltage increases, the total counts of reemitted positrons are gradually eliminated at the channeltron.

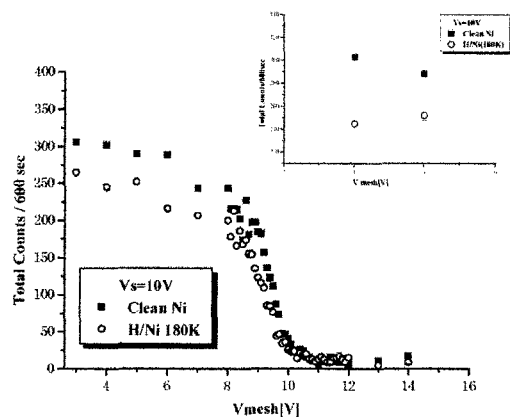


Fig.2 The number of reemitted slow-positron from the clean Ni(111) surface structure is disordered one of the β_1 state, as a function of the mesh voltage installed in front of the channeltron.

In this experiment, the sample voltage is 10V at constant and a positron beam of incident energy 1.99keV is incident on these surfaces. When -20V is imposed on the sample, a small number of positive particles (a few counts / 10min) are emitted from the samples. This means that the measured count about 3% as reflected positrons and relatively highly energetic hydrogen ions (above 20V). In the case of no positron incidence, the

background count is less than 0.005/min.

One of origins of the reduction of reemitted slow positrons might be due to the following mechanism. That is, the interaction between highly dense adsorbed hydrogen atoms and reemitted slow-positron might disturb strongly emission of thermalized slow positrons into vacuum.

Furthermore, in the case of hydrogen-saturated adsorbed Ni surface, a single vacancy in Ni is known to trap up to six H atoms [15]. As discussed by Fukai [16], in Ni, the binding energy amounts to 0.44eV for the first two H atoms and 0.28eV for the rest. Thus, the formation energy of a vacancy in Ni, $e_f=1.5\text{eV}$ [17], is effectively reduced to $e_f(\text{complex})=1.5-(0.44 \times 2+0.28 \times 4)=-0.50\text{eV}$, when H atoms are already present in solution. One of possible origins is that the hydrogen-induced vacancies might trap the thermalized positrons, in hydrogen-saturated adsorbed Ni surface such as β_1 state.

Another interesting origin is that the disordered structure of the β_1 state might contain many vacancy-like defects, which correspond to the positron-trapping sites.

The recent calculation [18] has shown that the Hydrogen-adsorption energies are much different in the low and high coverage case on Ni(111) surface. That is, in high coverage case, the repulsions between the adsorbed hydrogen increase remarkably. High repulsion energy might induce formation of the disordered structure of the β_1 state, which is different from the (2×2) -2H of the β_2 state. The present result suggests strongly that the disordering of the β_1 state is much related to formation of vacancy-like defects in its structure.

After measurement of clean Ni(111) surface for 5min are performed three times, the sample was annealed for 5min at 1140K to eliminate adsorption gas. After the Ni crystal is cooled to room temperature for 20min, hydrogen gas at $1.0 \times 10^{-8}\text{Torr}$ was introduced in the chamber for 5min for the adsorption of hydrogen atoms on the clean Ni(111) surface.

Fig.3 shows the total counts of the reemitted positrons of from the clean Ni(111) surface and the hydrogen-adsorbed Ni(111) surface, whose surface structure is the (2×2) -2H one of β_2 state, in the mesh voltage 4V and 5V at 240K.

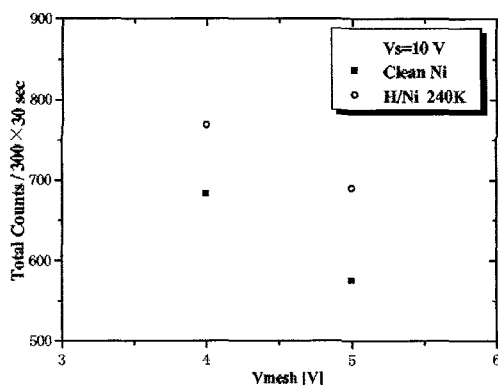


Fig.3 The total counts of the reemitted positrons from the clean Ni(111) surface and the hydrogen adsorbed Ni(111)

surface, surface structure is the (2×2) -2H one of β_2 in the mesh voltage 4V and 5V.

The number of the reemitted slow-positrons from the (2×2) -2H superstructure on Ni(111) surface is increased much in comparison with that from the clean Ni(111) surface. This means that the number of reemitted positrons from the surface changes drastically due to the effect of the adsorbed hydrogen.

In order to discuss this mechanism, we shall consider the electron work function ϕ_- and positron work function ϕ_+ on the hydrogen-adsorbed Ni surface. The electron work function ϕ_- for a solid is defined as the minimum energy required to remove a bulk electron from a point inside to one just outside the surface. This includes a bulk contribution, which is the electron's chemical potential μ_- , and the surface dipole barrier D . The dipole is primarily caused by the tailing of the electron distribution into the vacuum. The positron work function ϕ_+ is defined in the same way as the electron work function ϕ_- , where μ_+ is defined as the difference between the bottom of the lowest positron band and the crystal zero level [19]. The contribution to μ_+ includes repulsion from the ion cores and attraction to the electrons. The effect of the dipole D is positive for electron and negative for positrons. These contributions to the work function are given by

$$\phi_+ = -D - \mu_+ \quad (3)$$

$$\phi_- = +D - \mu_- \quad (4)$$

from eqs.(3) and (4), we can get the eq.(5) as follows,

$$\phi_+ = -\phi_- - \mu_+ - \mu_- \quad (5)$$

Murray and Mills [20] have shown that the reemitted positron yield increases as ϕ_+ becomes more negative for many metals. Chemisorption of hydrogen on Ni surfaces causes an increase of the electron work function ϕ_- . This represents that the adsorbed hydrogen become negatively polarized. The maximum change, $\Delta\phi_{-max}$ found with polycrystalline Ni surface line in the range of about 0.35eV [21]. K.Christman et.al. [3] have reported that the maximum increases, 0.195, 0.170, and 0.530eV, of the electron work function were observed with Ni(111), (100), (110), respectively.

Furthermore, an almost linear increase of the electron work function is observed up to 0.5ML coverage in the (2×2) -2H superstructure on Ni(111) experimentally [3]. Theoretically the same dependence is calculated [8].

From eq.(5), it is derived that the positron work function ϕ_+ becomes more negative when the electron work function ϕ_- increase due to the hydron-adsorbing. Thus we can understand that the reemitted slow positron yield from the (2×2) -2H Ni(111) superstructure increases in comparison with that from clean Ni(111), because the positron work function ϕ_+ becomes more negative.

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