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Spin-polarized ion scattering spectroscopy of CCl_4 adsorption on Fe(001) surfaces

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ABSTRACT

The interaction of CCl_4 molecules with Fe(001) surfaces was investigated by spin-polarized ion scattering spectroscopy (SP-ISS). It was observed that CCl_4 molecules adsorb dissociatively on the surface at ambient temperature (~290 K), and consequently, iron and chlorine were major surface constituents. It was found that the chlorine adatoms are located atop of iron atoms of the second surface layer (hollow sites of the surface). It is indicated that the spin state of iron atoms at the surface is not affected by exposure to a CCl_4 atmosphere, while almost no spin is induced in the chlorine adatoms. Similar behavior is observed in the spin states of iron and chlorine on an oxygen preadsorbed-Fe(001) surface. The difference in the spin states of iron and chlorine clarifies the local property of the incidence ion neutralization and element selectivity of SP-ISS in this CCl_4/Fe system.

1. Introduction

We recently reported the development of spin-polarized ion scattering spectroscopy (SP-ISS) as a novel method for analyzing surface magnetic structures [1,2]. In SP-ISS, electron spin-polarized $^4He^+$ ions are projected on sample surfaces, and the kinetic energy of scattered ions is analyzed. The typical kinetic energy of the incident He^+ ions is in the order of keV, and therefore, most incident He^+ ions are neutralized at the sample surface [3]. Since SP-ISS detects the scattered He^+ ions that survived this efficient neutralization at the surface, it has extreme surface sensitivity as conventional ISS (also called low-energy ion scattering (LEIS)) with a He^+ ion beam as a probe. Thus, only a few layers of the surface are selectively observed in SP-ISS. This surface sensitivity of SP-ISS is strikingly different from other well-known element selective methods, such as X-ray magnetic circular dichroism.

The neutralization of the incident He^+ ions typically occurs by the transition of a surface electron to a 1s hole of the incident He^+ ion (Auger neutralization (AN)) [4]. Since the spin of a surface electron filling the hole in the He^+ ion 1s orbital should be anti-parallel to that of the He^+ 1s electron according to the Pauli exclusion principle in this AN process [5], the scattered He^+ ion intensity is different between the case in which the He^+ spin is parallel to majority spins of the surface and the case in which the He^+ spin is parallel to minority spins of the surface. Moreover, ion neutralization reflects the electronic state of target atoms involved in collisions with the incident He^+ ions. The kinetic energy of the scattered ions depends on the mass of the target atoms; therefore, element selective spin state analysis at outermost surfaces can be possible by measuring the spin dependence of the neutralization probability of the incident He^+ ions as a function of the kinetic energy of scattered ions. In fact, we have shown the possibility of element selective spin state analysis of SP-ISS on Fe(001) surfaces exposed to an O_2 atmosphere in our previous study [1].

The element selectivity of SP-ISS, which is an important feature in magnetic structure analysis, is derived from the local character of AN. Therefore, it depends on the electronic structure of the sample surfaces, although the local character of AN is still not fully understood [6,7]. For example, element selectivity of SP-ISS is expected on surfaces with localized electronic states. One of straightforward methods for demonstrating the element selectivity of SP-ISS is to show clear element dependence of spin states detected in SP-ISS.

In this study, we show the SP-ISS data of Fe(001) surfaces exposed to a carbon tetrachloride (CCl_4) atmosphere. We found that almost no spin is induced in chlorine adatoms, while iron has a negative spin state at the Fermi level, where a positive (negative) spin state is defined as the state in which a number of majority spins is larger (smaller) than that of minority spins. These results indicate the local character of AN and the element selectivity of SP-ISS in this CCl_4/Fe(001) system.

The absorption of carbon tetrachloride on solid surfaces has attracted attention, because such systems are important in tribology. Carbon tetrachloride has been used as an additive in lubricants

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which work in extreme pressure conditions. Therefore, it is useful in the cutting and grinding of metals, although it is now known that carbon tetrachloride causes adverse health effects [8]. The role of the lubricant additives and the mode of tribological activity have been discussed through studies concerning the interaction of carbon tetrachloride molecules with clean metal surfaces in ultrahigh vacuum (UHV) [9–12].

In these studies, it has been generally observed that CCl_4 adsorbs dissociatively on iron surfaces at ambient temperature. For example, Jones discussed surface structures at elevated temperature followed by dissociative absorption of CCl_4 on Fe(001) at ambient temperature [9]. Smentkowski et al. identified molecular products followed by the dissociation of CCl_4 on Fe(110) surfaces in the temperature range between 90 and 1050 K [10–12]. They reported iron chloride species of unknown stoichiometry is formed at the surface by the exposure at 300 K, which is stable up to 900 K. The identification of this high temperature product of iron chloride is important for understanding the role of the CCl_4 additives in lubricants. In fact, several groups have studied high temperature products at CCl_4/Fe interfaces [13].

In this study, the structure and the composition of Fe(001) surfaces exposed to CCl_4 at ambient temperature was analyzed by ISS. As reported earlier by several groups, it was observed that CCl_4 decomposed on the surface, and consequently, the major constituent elements at the outermost surface were iron and chlorine. It was found that the chlorine adatoms were located at atop of iron atoms in the second surface layer (hollow sites of the surface). We interpret that this structure corresponds to that of the high temperature product of iron chloride mentioned above. The present SP-ISS result indicates that almost no spin is induced in the chlorine adatoms in the hollow sites of the outermost surface.

2. Experimental method and set-up

2.1. CCl_4/Fe(001) samples

The experiments were performed in an UHV chamber (base pressure of 5×10^{-11} Torr). We grew bcc-Fe(001) films epitaxially on MgO(001) single-crystalline substrates by vapor deposition, where the epitaxial orientation relationship is Fe(001)//MgO(001) and Fe[110]//MgO[100] [14]. We purified CCl_4 (Junsei, purity 99.5+%) by several freeze–pump–thaw cycles, and introduced it into the vacuum chamber via a variable leak valve, while the temperature of the iron substrate was maintained at ambient temperature (~290 K). Exposures to CCl_4 are quoted in Langmuirs ($1\,\mathrm{L} = 1 \times 10^{-6}$ Torr s) in this paper, where values are calculated using uncorrected ion gauge readings.

2.2. SP-ISS

In SP-ISS, spin-polarized He^+ ions were projected on sample surfaces, and the intensity of scattered He^+ ions was measured using an electrostatic energy analyzer [1,2]. The spin direction of the incident He^+ ions was either parallel or anti-parallel to majority spins of the samples.

The details of our experimental set-up have been described elsewhere [1,2,17]. Thus, only essence and a new modification of our apparatus are focused below.

The spin-polarized He^+ ions were generated from Penning ionization of spin-polarized He 2^3S_1 atoms (He^*), which were generated in an RF discharge [15,16]. The spin polarization of He^* was performed by optical pumping (OP) [17]. The kinetic energy of the incident He^+ ions and scattering angle were set to 1.41 keV and 150° in the present study. The spin direction and polarization of the He^+ ions were determined from the comparisons of emitted electron spectra between He^+ and He^* [18]. The sample was pulse-magnetized in-plane prior to measurements, where the magnetization direction was parallel to the Fe[010] easy axis. Both the incident and exit directions of the He^+ ions were perpendicular to the magnetization, and therefore, the scattering plane contained the surface normal. The SP-ISS spectra were obtained using a rotatable hemispherical sector analyzer (Omicron SHA50). The measurements were performed in a constant pass energy mode. The pass energy was set to 40 eV in ISS and 318 eV in SP-ISS.

In this study, the discharge bulb was improved as described below. In our previous study, it was revealed that the degree of circular polarization of the OP radiation fairly affects the polarization of $He^*(P_{He^*})$, and thus, the polarization of He^+ (P_{He^+}) [2]. It is well-known that the depolarization of light with circular polarization occurs when the light passes through non-perpendicular glass plates. In order to avoid such depolarization, the discharge bulb was redesigned as shown in Fig. 1. This improved version of the discharge bulb has a flat window for the OP radiation of the σ pumping, whose normal direction is parallel to the OP radiation. The bottom of the discharge bulb has also a similar plane shape window to suppress depolarization of the reflected light. The diameter of the window is approximately 5 cm. The performance of this discharge bulb is summarized in Fig. 2, where (P_{He^+}) is plotted as a function of the OP radiation density. It is observed that (P_{He^+}) increases rapidly with increasing OP radiation density in the range from 0 to 0.05 W/cm^2, while it is almost constant above this range. On the other hand, (P_{He^+}) decreased above 0.05 W/cm^2 using the discharge bulb of our former version, which had a round cross sectional shape. We have discussed that this decrease of (P_{He^+}) was due to imperfect polarization of the OP radiation from a rate equation analysis [2]. This decrease of (P_{He^+}) is successfully suppressed with the improved discharge bulb, as shown in Fig. 2, suggesting that imperfect polarization, which causes a decrease in (P_{He^+}) with the intense OP radiation density, is due to depolarization of σ radiation at the bulb wall. With an RF power of 3 W, a pressure of 18 Pa, and an OP radiation density of 0.05 W/cm^2, (P_{He^+}) was 19%

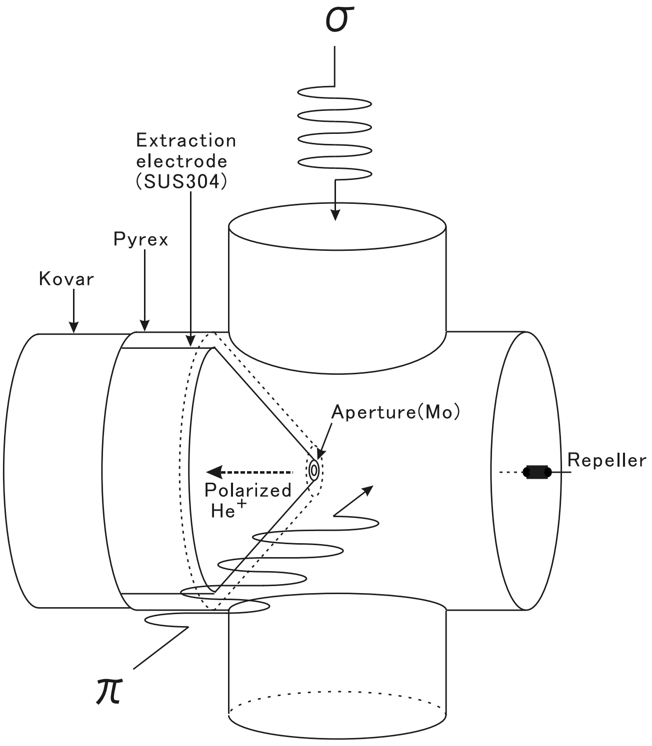

Fig. 1. Schematic of the improved RF discharge bulb.