

INVESTIGATION OF GAS SPECIES GENERATED IN THE PHOTOEMISSION SPECTROSCOPY SYSTEM AT THE SIAM PHOTON LABORATORY

Wiwat Wongkokua¹ and Prayoon Songsiriritthigul^{2,3*}

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Abstract

This report describes the design of the vacuum system of the photoemission spectroscopy system installed at the first beamline of the Siam Photon Laboratory, and shows the results from the investigation of gas species generated in the system. The base vacuum pressure of the system after the well bake-out processes is approximately 2×10^{-10} mbar. The vacuum pressure increases more than one order of magnitude when there is a linear movement of the sample manipulator or when the UV lamp, the electron gun or the X-ray source is operated. The gas species generated in the system were analyzed by the quadrupole mass spectrometer. Adsorption of the gas molecules on a clean well-defined Ni(111) surface has been observed by low-energy electron diffraction and Auger electron spectroscopy measurements.

Introduction

In the investigation of the electronic structures of surfaces of solids, good vacuum conditions have to be maintained to prevent contaminations on the surfaces. It is well-known that even at the pressure of 1×10^{-6} mbar, residual gases can theoretically form a monolayer of coverage on a clean surface within one second at room temperature assuming that the sticking coefficient equals 1.0 (Hoffman *et al.*, 1998). At lower pressures, the time for forming a monolayer of coverage becomes longer. To obtain invaluable information of surfaces, the time required for gases to form a monolayer of coverage must be

much longer than the time required for the measurement. Thus the vacuum pressure required for research on the electronic structures of surfaces of solids must be in the range of 10^{-10} mbar or lower. With the current vacuum technology, a base vacuum pressure of 10^{-10} mbar can be produced without great difficulties by reducing the out gassing rate of the chambers and vacuum components (Readhead, 1996; Readhead, 2002). However, it is difficult to maintain the vacuum in any measurement system at this pressure when an excitation source such as an X-ray source, an electron gun or a UV

¹ Graduate Student, School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000

² Ph.D., Lecturer, School of Physics, Institute of Science, Suranaree University of Technology, Nakhon Ratchasima, 30000

³ National Synchrotron Research Center, Nakhon Ratchasima, 30000

* Corresponding author

discharge lamp is used in the measurement. At the Siam Photon Laboratory, the experimental station of BL-4 beamline is an electron spectroscopy system designed for the investigation of the electronic structure of bulk and surface of solids (Songsiririthigul *et al.*, 2000). Thus, it is especially important for this work to investigate the production of gases in the experimental system in order to understand the performance of the system limited by its vacuum conditions.

Description of the Vacuum System

Figure 1 shows the photo of the electron spectroscopy system installed at the first beamline of the Siam Photon Laboratory. The main analysis tools are two electron energy analyzers, one is a Thermo VG Scientific ARUPS10 to be used for angle-resolved photoemission measurements, and the other is a Thermo VG Scientific CLAM2 to be used for angle-integrated photoemission measurements. The system is also equipped with an electron gun, a twin anode X-ray source, a UV discharge lamp and a low-energy electron diffractometer. This provides the possibility to perform different surface analysis measurements such as XPS

(X-ray photoelectron spectroscopy), UPS (ultraviolet photoelectron spectroscopy), AES (Auger electron spectroscopy) and LEED (low-energy electron diffraction) measurements. More importantly, the system is connected to the first beamline of the Siam Photon Laboratory, allowing photoemission experiments using synchrotron light in the energy range of 20-240 eV to be performed.

Figure 2 shows the diagram of the vacuum system of the electron spectroscopy system. The system consists of three main vacuum chambers, i.e. an analysis chamber, a preparation chamber and a fast-entry-air-lock (FEAL) chamber. The three chambers are vacuum-isolated by two UHV manual gate valves (V1 and V14). All the excitation sources, analysis tools and the quadrupole mass spectrometer (QMS) are installed in the analysis chamber which is made of μ -metal to reduce the disturbance of the motion of photoelectrons from external magnetic fields. The rest are made of the 304 stainless steel because of an ease of fabrication and economic reasons.

QMS provides a way to quantitatively analyze gas species with mass between 1 amu and 100 amu in the system. The partial pressure

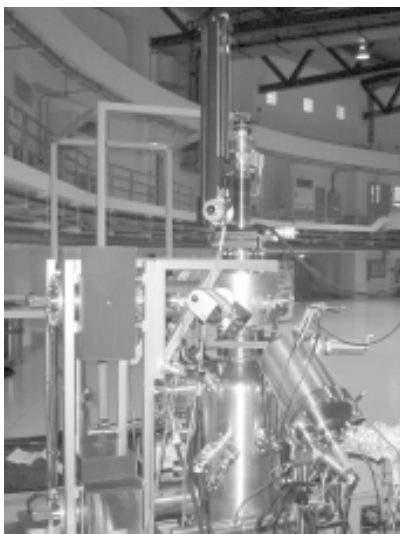


Figure 1. The photoemission system at the Siam Photon Laboratory

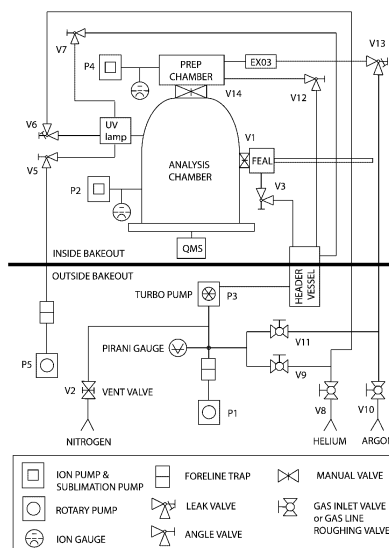


Figure 2. Schematic diagram of the vacuum system of the photoemission system

of different gases in the system can also be calculated based on the assumption that the summation of the partial pressures of all gases with mass less than 100 amu equals the total pressure measured by the Bayard-Alpert (B-A) gauge. The principle of operation for QMS can be summarized as follows. The neutral gases in a vacuum system are ionized by low-energy electron at one end of QMS. The ions are extracted into a region with a high frequency quadrupole field where the ions are distinguished by their mass-to-charge ratio. After that, the ions are detected by either a Faraday cup or a continuous dynode secondary electron multiplier installed at the other end of QMS.

Samples can be introduced into the analysis chamber via the FEAL without breaking UHV condition, the typical pressure during transferring samples is about 5×10^{-8} mbar. The sample manipulator is vertically mounted on top of the preparation chamber. The vertical linear motion of the manipulator provides the possibility to move the samples between the preparation chamber and the analysis chamber. The samples can be cleaned by either electron bombardment heating or argon ion sputtering in the preparation chamber with the V1 isolation valve closed. This is to prevent contamination in the analysis chamber.

In the initial pumping procedure, the whole system is evacuated by a 250 l/s turbo molecular pump (P3) backed by a rotary pump (P1). To achieve ultimate vacuum pressure, a 240 l/s ion pump (P4) with integral titanium sublimation pump (TSP) and a 480 l/s ion pump (P2) with integral TSP are used in the preparation chamber and the analysis chamber, respectively. The UV lamp requires a two-stage differential pumping system, which is provided by the turbo molecular pumping unit (P3 & P1) and an additional rotary pump (P5). The vacuum pressure of the preparation chamber and the analysis chamber are measured by B-A gauges.

Materials and Methods

In the production of UHV in the range of 10^{-10} mbar, the baking procedures for the electron

spectroscopy system are essential to remove adsorbed gas molecules on the inner wall of the vacuum chamber and on the surface of components in the vacuum system. The whole system was baked in an aluminum case at 150 °C for 72 h. During the baking, desorbed gas molecules were evacuated by the turbo-molecular pumping unit, P3 & P1. The filaments of all instruments installed in the system were well-degassed while the temperature of the system was above 100 °C. Degassing of the filaments was carried out by direct heating with a *dc* current passing through the filaments.

The gas species generated during the operation of the X-ray source, the UV discharged lamp and TPS were analyzed by QMS, which was also used to monitor the variations of the amount of gases in the system during the movement of the mechanical components such as the sample manipulator, the gate valve and the goniometer of the ARUP10 analyzer. The partial pressures of different gases have also been calculated by using the results obtained from QMS.

The study of adsorption of gas molecules on a clean metallic surface has been carried out. A clean single crystal Ni(111) surface was prepared by heating at 750 °C and Ar⁺ ion sputtering repeatedly. Impurities on the surface were below the detection limit of AES. LEED has also been used to confirm the well-defined surface. The clean surfaces exposed to the residual gases at base pressure and to the gases generated during operating the UV lamp have been investigated.

Results and Discussion

After the bake-out and degassed procedures, the ultimate vacuum pressure of approximately 2×10^{-10} mbar in the preparation and analysis chambers has been obtained. QMS with a continuous dynode secondary electron multiplier was used to analyze the residual gases in the system. Figure 3 shows the spectrum from the measurements using QMS. The spectrum is complicated due to the fact that ionization of molecules consisting of different

kinds of elements result in a number of possible kinds of ions, and the fact that the fragment ions appear in singly and multiply charged molecule ions. The gas species were identified as H_2 , He, CH_4 , H_2O , CO/N_2 , Ar and CO_2 . The main gas species was H_2 with the partial pressure of 6.6×10^{-11} mbar. It should be noted that CO and N_2 have same mass. Thus, the two species cannot be distinguished.

Figure 4 shows the variation of H_2 , CO/N_2 and CO_2 in the system during the operation of TSP (A), closing and opening operations of the V14 isolation gate valve between the preparation and analysis chambers (B and C, respectively), 600 mm vertical translation of the manipulator relocating the sample holder from the preparation chamber to the analysis chamber (D), *theta*-rotation and *phi*-rotation of the ARUPS10 analyzer (E and F respectively). When TSP was turned on, the vacuum pressure measured by the B-A gauges increased about one order of magnitude. It is obvious from the measurement using QMS that the increase of the pressure was caused mainly by the increase of the amount of H_2 released from the filament of TSP, as shown in Figure 4. The closing and opening operations of the V14 valve also introduced gases into the system. However, the amount of gases was not significant since the time interval for these actions was rather short. During the movement of the manipulator (indicated by the D interval), the partial pressure of all monitored gases

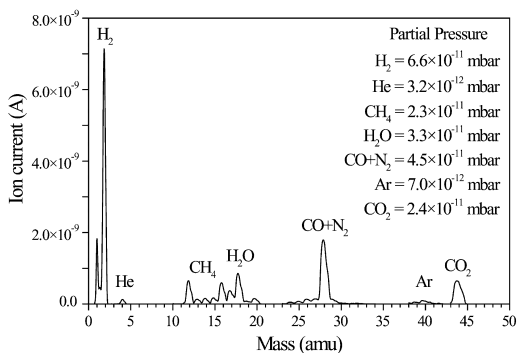


Figure 3. QMS spectrum was taken with a mass scan mode showing gas species in the photoemission system at the base pressure of 2×10^{-10} mbar

increased to the same magnitude. The total pressure measured by the B-A gauges increased about one order of magnitude. It is interesting to observe that the pressures fluctuated with time though the movement was smoothly and continuously driven by a stepper motor. The spectrum of the gases during the translation of the manipulator is also shown in Figure 5. CO/N_2 and CO_2 were found to increase relatively much higher than the other gases. As shown in Figure 4, the time required to move the sample down from the preparation chamber to the analysis chamber was about 3 min. A large amount of gases was produced in the system, and thus a long period of time was required to restore the vacuum pressure suitable for the surface analysis measurements. Figure 4 also shows that the rotations of the ARUP10 analyzer caused the production of gases in the system, indicated by the E and F intervals.

The production of gases in the system during the operation of excitation sources has also been examined. Figure 6 shows the spectrum measured during the operation of the UV discharged lamp. The total pressure in the analysis chamber was 2×10^{-8} mbar when He I (21.2 eV) radiation was produced. Helium was the main gas species found in the system as

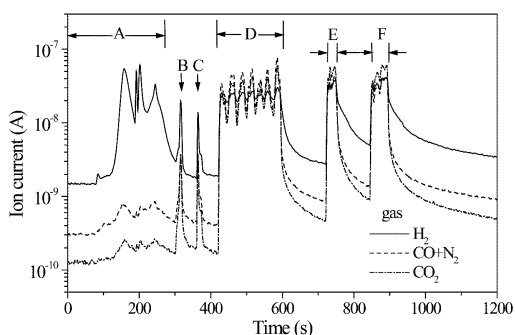


Figure 4. QMS spectra were taken with a time scan mode showing gases generated in the photoemission system during the operation of TSPs (A), closing and opening the V14 gate valve (B and C, respectively), Z-motion of the sample manipulator (D), *theta*- and *phi*-rotations of ARUPS10 (E and F, respectively)

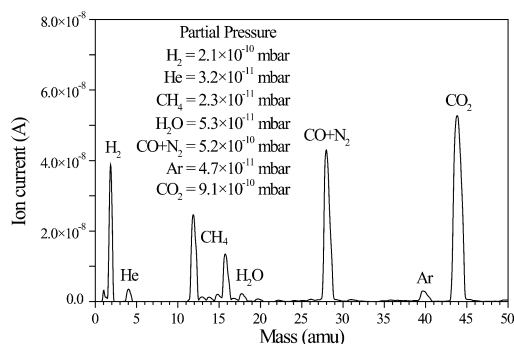


Figure 5. QMS spectrum was taken with a mass scan mode during the sample was being transported from the preparation chamber to the analysis chamber. The average total pressure was 2×10^{-9} mbar

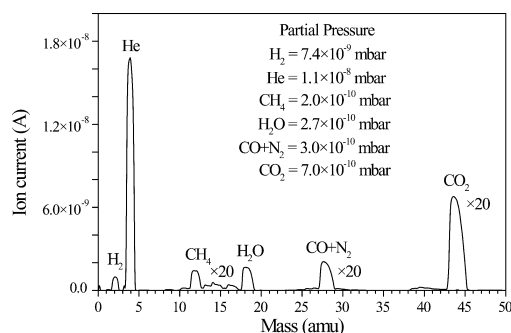


Figure 6. QMS spectrum was taken with a mass scan mode during the operation of the UV lamp. The total pressure was 2×10^{-8} mbar

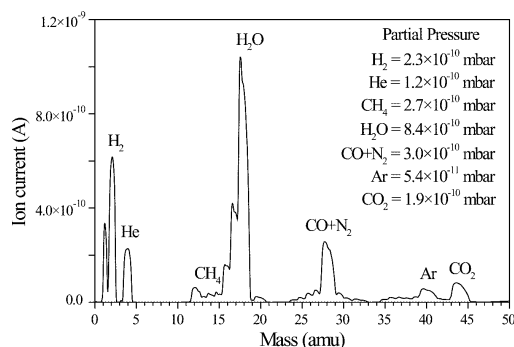


Figure 7. QMS spectrum was taken with a mass scan mode during the operation of the X-ray source. The total pressure was 2×10^{-9} mbar

expected. This is a drawback of using UV discharge lamps for very reactive surface samples since some gases generated in the discharge region may be transported into the analysis chamber through a capillary tube. Thus the samples may be exposed to those gases from the discharge region causing the surface being analyzed to be contaminated. Another problem caused by using helium in UV discharge lamps is that it takes a long time, 3-4 days for this system, to recover vacuum conditions. This is due to the fact that pumping efficiency of nearly all kinds of vacuum pumps for inert gases is rather low.

While the X-ray tube was operated, the pressure rose to about 2×10^{-9} mbar. The gases in the system identified by QMS are shown in the spectrum in Figure 7. The main gas species was H_2O instead of H_2 , indicating that there was a very small leakage of cooling water into the system. This also explains the presence of H_2O in the system after the baking and degassing procedures as the leakage also occurred during degassing the filament on the X-ray source.

After several months cleaning routine, by repeated heating and Ar^+ ion sputtering, no impurity on the surface of Ni(111) sample was detected by AES measurements. AES spectrum in Figure 8(a) shows that the impurity level is below the sensitivity of the AES measurements. From LEED studies, as shown by the sharp (1×1) LEED pattern in Figure 8(b), a well-defined (111) surface has been obtained. However, after the cleaned well-defined Ni(111) sample has been left in the analysis chamber at the base pressure of 2×10^{-10} mbar for four days, gases are adsorbed on the surface of the sample. This is confirmed by the AES and LEED measurements. The obtained AES and LEED results are shown in Figures 9(a) and 9(b), respectively. The observed impurities on the surface were identified as C, N and O with the atomic concentration of 5.4%, 2.4% and 3.9%, respectively. The LEED pattern became unclear, indicating the disorder of the atomic arrangement at the surface of the sample.

Figures 10(a) and 10(b) are the AES spectra and the LEED pattern respectively taken

from the clean and well-defined Ni(111) sample after the sample has been measured by UPS technique using the discharged He lamp as a UV light source for one hour. Since the vacuum pressure in the analysis was rather high (2.5×10^{-8} mbar) during the operation the UV lamp, it was not surprising at all to observe that the sample became contaminated during the UPS study. The main impurities were C, N and O with atomic concentration of 5.7%, 1.1% and 1.7%,

respectively. These impurities were generated in the discharged region, and transported through the capillary tube of the UV lamp into the analysis chamber. This should be taken into consideration when the photoemission measurements using the discharged UV lamp are performed, especially on chemically reactive materials. To alleviate the effects from the surface contamination, a short measurement time may be necessary, and this has to be traded

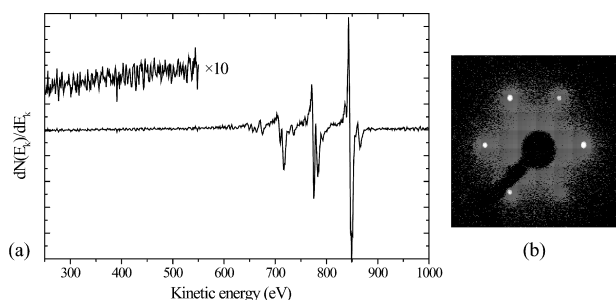


Figure 8. AES spectrum (a) and LEED pattern (b) of a clean well-defined Ni(111)

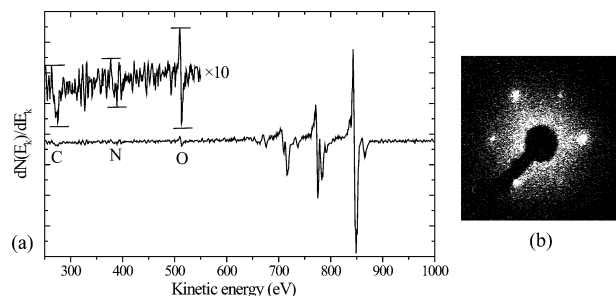


Figure 9. AES spectrum (a) and LEED pattern (b) of a clean and well-defined Ni(111) sample after four days being left in UHV at the pressure of 2×10^{-10} mbar

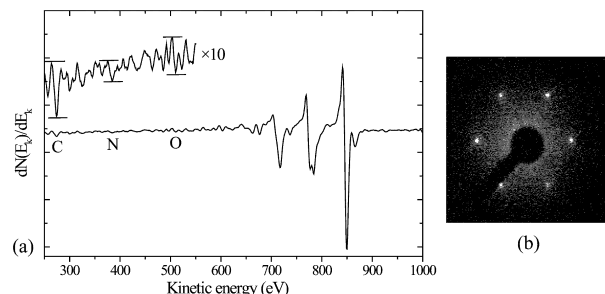


Figure 10. AES spectrum (a) and LEED pattern (b) of clean and well-defined Ni(111) sample after a one-hour operation of the UV lamp

off with the spectral resolution.

However, as mentioned above, the photoemission system is connected to the synchrotron light beamline which acts as one of the excitation sources. No rising of the vacuum pressure in the analysis chamber occurs during the photoemission measurements using monochromatized synchrotron light. Thus, the measurements are performed at the base pressure of the system, at 2×10^{-10} mbar. At this pressure, the time required for forming a monolayer of adsorbed gases is theoretically more than an hour; therefore, a plenty of time is available for the measurement before the surface becomes contaminated. In fact, for some materials such as Ni, the measurement time can last up to 6 h before the surface contamination could be detected by AES. The results from the studies of Ni(111) has been reported elsewhere (Warwick *et al.*, 2004).

Conclusion

We have investigated the production of gases in the photoemission spectroscopy system of the BL-4 beamline at the Siam Photon Laboratory. The contamination on the surface of the samples by the generated gases has also been studied. The gas species detected at the base pressure were H₂, He, CH₄, H₂O, CO/N₂, Ar and CO₂. Movements of the mechanical parts in the system such as valves and the translator of the manipulator generated additional gases in the system. The operation of TSP and the laboratory excitation sources also increase of the vacuum pressure. The UV lamp and X-ray source must

be used in measurements with caution that a large amount of gases is generated, resulting in the contamination on the surface of the samples. The monochromatized synchrotron light has been proven to be clean, causing no contamination on the surface of the samples.

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