7A/1999G078

Two distinct adsorption states of selenophene monolayer on Au(111)

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Introduction

Selenium-containing molecules are good candidates for formation of self-assembled monolayers on gold surfaces. A previous STM study of selenophene (C_4H_4Se) on Au(111) indicated that a well-ordered monolayer is formed by exposing the Au(111) surface to gaseous selenophene under atmospheric condition [1]. A theoretical study, however, claimed that thiophene (C_4H_4S), an analogue of selenophene, shows quite a weak chemical interaction with gold [2]. In fact, our thermal desorption study revealed that both thiophene and selenophene monolayers on Au(111) formed under ultrahigh vacuum (UHV) condition desorb below room temperature. In this work we studied selenopene monolayers on Au(111) prepared by vapor deposition under both atmospheric and UHV conditions by means of carbon K-edge near-edge x-ray absorption fine structure (NEXAFS) and x-ray photoelectron spectroscopy (XPS) to understand interactions of selenophene with gold.

Experimental

The C K-edge NEXAFS and XP spectra were taken at BL-7A. Au(111) surfaces were prepared by thermally evaporating gold onto cleaved mica. Two types of selenophene monolayers were prepared by exposing the clean surfaces to gaseous selenophene under UHV condition at 215K (UHV phase) and under atmospheric condition at room temperature (atmospheric phase). In addition we measured a Se 3p XP spectrum of a CH_3Se monolayer as the standard.

Results and discussion

Fig. 1-b shows C K-edge NEXAFS spectra for the UHV phase. The ratio of the intensity of the π^*_1 peak to the edge jump is a little smaller than that of a multilayer (Fig. 1-a), though the peak positions are the same. This indicates that selenophene molecules in a monolayer in the UHV phase are not dissociated but molecularly chemisorbed to the substrate only by partial back donation to the π^*state. The aromatic ring lies parallel to the substrate as is indicated by the polarization dependence. After annealing the surface to room temperature no C or Se was detected by XPS. These observations agree with the theoretical prediction for a weak interaction mentioned above. Se $3p_{3/2}$ XPS peak for this phase was observed at 162.0 eV.

For the atmospheric phase Se $3p_{3/2}$ XPS peak was obserbed at 160.5 eV [1]. This peak position is significantly different from that of the UHV phase, but identical with that of CH_3Se-Au species. These results suggest that the Se atom is covalently bonded to the Au atom(s) in the form of a selenolate, implying that the selenophene molecules are dissociatively adsorbed on Au(111) under atmospheric condition. The NEXAFS spectra for the atmospheric phase are shown in Fig.1-c. They are quite different from those for the UHV phase both in shape and in polarization dependence. The existence of two π^* peaks represents that the butadiene structure in the molecule is retained. The orientation angle is estimated to be $43\pm10^\circ$ from the surface normal. The intensity of the π^*_1 peak compared to the edge jump is much smaller than that of the UHV phase. The significant reduction in intensity of the π^*_1 peak was also observed for C_4H_4-Pd metallacycle [3]. The results of XPS and NEXAFS suggest that a metallacycle-like species containing a Se-Au bond is formed in the case of atmospheric phase. The dissociative adsorption takes place probably through trapping-mediated adsorption where physisorbed layers play a key role to reduce the potential barrier to dissociation. The high pressure of gaseous selenophene under atmospheric condition might cause a considerable increase in residence time of the physisorbed layers.

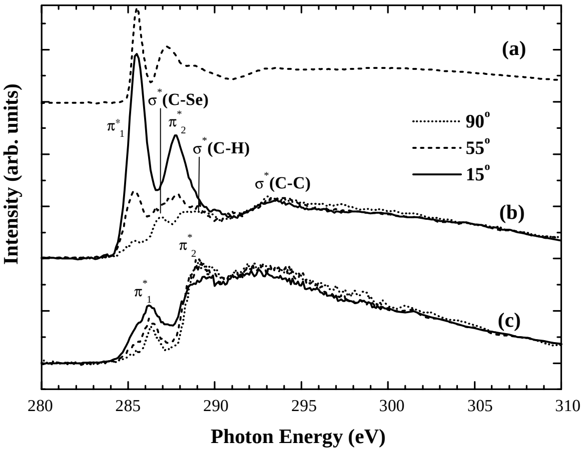

Fig. 1: C K-edge NEXAFS spectra for selenophene on Au(111) (a) multilayer, (b) monolayer prepared under UHV condition and (c) monolayer prepared under atmospheric condition

References

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