

## Tetrathiafulvalene on ZnO : Surface Termination Dependence of Adsorption State Studied by PES and XAS

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### Introduction

Tetrathiafulvalene (TTF) is a prototype charge-donor molecule in organic charge-transfer salts. One of the characteristics of TTF is that variety of TTF-derivatives can be synthesized. Thus, TTF and its derivatives should be a good choice to functionalized solid surfaces. Moreover, utilizing donating character of TTF and its derivatives, it is possible to control charge density of semiconductor surfaces. However, only a few study has been done so far for the TTF adsorption systems. In the present study, we examine the TTF-adsorbed ZnO surfaces by means of photoelectron spectroscopy (PES) and x-ray absorption spectroscopy (XAS) and show how

surface termination affects the adsorption structure of TTF on the ZnO surface.

### Experimental

The PES and XAS measurements were carried out at beamline 13A of the Photon Factory, KEK. Single crystal ZnO surfaces with (10-10), (000-1) and (0001) orientation were cleaned in the ultrahigh vacuum chamber by cycles of Ar<sup>+</sup> sputtering and annealing. TTF was dosed on the ZnO surfaces using a home-made evaporator. TTF adsorption and PES and XAS measurements were done at the substrate temperature of 300 K.

### Results and Discussion

Adsorption of TTF on the ZnO surfaces reaches saturation at room temperature. The saturation coverages [ $1.6 \times 10^{14}$ ,  $1.3 \times 10^{14}$  and  $0.5 \times 10^{14}$  cm<sup>-2</sup> for ZnO(0001), (10-10) and (000-1), respectively] are proportional to the Zn concentrations of the substrate surfaces. This means that TTF interacts with the surface Zn atoms. Fig. 1 shows the S 2p spectra for three adsorption systems. Aside from the emission intensity, the spectral lineshape depends strongly on the surface termination, indicating the multiple components with varying intensity ratios. Deconvolution of the spectra reveals that there exist three species on the surface, and, from their peak positions, they are assigned to neutral TTF (TTF<sup>0</sup>), negatively charged TTF (TTF<sup>-</sup>) and decomposed S-containing species. The formation of the negatively charged TTF is surprising since TTF usually acts as a charge donor when interacting with other species.

The ratio of decomposed species to molecularly adsorbed TTF (TTF<sup>0</sup>+TTF<sup>-</sup>) increases with increasing the surface O concentration. This implies a certain role of the O atoms in TTF dissociation. Fig. 2 displays a possible initial dissociation process on ZnO(000-1). TTF adsorbs at the step edges on the surface where the Zn atoms are exposed by forming the Zn-S bond. At the same time, hydrogen bonds are expected between H of TTF and substrate O. This hydrogen bonding may lead to deprotonation, which is followed by further decomposition of TTF.

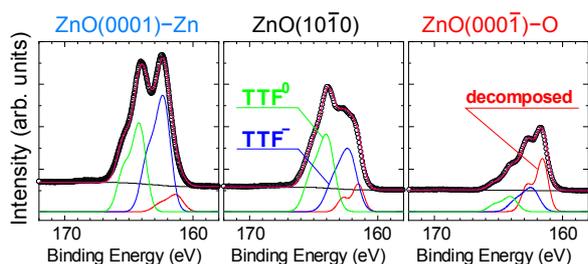


Fig. 1 S 2p spectra of TTF on three ZnO surfaces. Peaks are composed of three components associated with TTF<sup>0</sup>, TTF<sup>-</sup> and decomposed TTF.

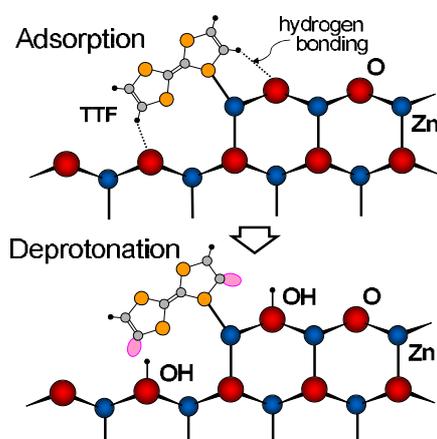


Fig. 2 Possible initial decomposition process, i.e. deprotonation, of adsorbed TTF on ZnO(000-1).

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