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Electronic structure and ultrafast charge carrier dynamics of Zn clusters supported on a p-Si(100) surface

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Abstract

Femtosecond XUV photoemission spectroscopy is employed to monitor the non-metal to metal transition of Zn clusters grown on p-Si(100) as well as the ultrafast charge migration, trapping, and recombination at the surface.

Introduction

Nanostructured materials consisting of semiconductor substrates decorated with small clusters and nanoparticle have many potential photocatalytic applications such as generation of storable fuels from sustainable inputs, antibacterial action, and degradation of organic pollutants. The fate of a photocatalytic reaction is drastically influenced by the electronic structure of the cluster as well as the energy band alignment between the cluster and surface. Understanding the electronic structure and ultrafast photoinduced charge carrier dynamics at the cluster-surface interface is a defining principle that will guide advances in the field of photocatalysts.

Time resolution, surface sensitivity and element specificity are technical ingredients required to investigate ultrafast photoinduced processes of charge migration, localization and recombination at the surface of photocatalytic materials. All these requirements are fulfilled by an experimental technique based on pump-probe photoelectron spectroscopy in conjunction with femtosecond extreme ultraviolet (XUV) laser pulses. In this work, we discuss recent breakthroughs in measuring electronic structure and ultrafast charge carrier dynamics at the surface of a model photocatalytic system consisting of a p-type doped Si(100) surface decorated with Zn clusters. Static XUV photoemission spectroscopy is utilized to monitor the electronic structure of Zn clusters on p-Si(100) as a function of Zn deposition. The transition from non-metallic to metallic Zn character is observed at 0.16 ML of Zn coverage. Furthermore, the femtosecond pump-probe XUV photoemission spectroscopy technique is employed to induce a charge transfer from the p-Si(100) substrate to the Zn clusters and to measure in real time the charge trapping at the Zn cluster as well as the subsequent charge relaxation. The ultrafast charge carrier dynamics is investigated as the Zn dimensionality is increased from small clusters composed of a very few atoms to large particles to extended Zn films.

Results

Model photocatalysts consisting of Zn clusters supported on a p-Si(100) substrate are prepared and their electronic structure and ultrafast electron dynamics are investigated. The Zn clusters are produced by evaporating well-defined amounts of Zn on the p-Si(100) surface at 90 K. Figure 1 displays photoemission spectra obtained from various amounts of Zn evaporated on the p-Si(100) surface. A distinct peak originating from the Zn 3d electronic states is observed at a binding energy of -10 eV. By increasing the amount of Zn on the p-Si(100) surface, the Zn 3d photoemission peak intensity increases and shifts to lower binding energy. To investigate the electronic structure of the Zn clusters, the photoemission obtained from the bare Si(100) substrate is subtracted from the photoemission spectra obtained with various amounts of Zn on Si(100) (cf. inset in Figure 1). At low Zn coverage of 0.02-0.12 monolayer equivalent (ML), the photoemission onset starting below the Fermi level (0 eV) indicates that non-metallic Zn clusters are formed. At Zn coverages higher than 0.16 ML, the photoemission onset starts at the Fermi level indicating that the Zn clusters have a metallic character.

Femtosecond pump-probe XUV photoemission spectroscopy [1] is employed to induce a charge transfer from the p-Si(100) substrate to the Zn clusters and to measure in real time the charge trapping at the Zn cluster as well as the subsequent charge relaxation. The ultrafast charge carrier dynamics is investigated as the Zn dimensionality is increased from small clusters composed of a very few atoms to large particles to extended Zn films. Figure 2 displays

Figure 1. Photoemission spectra obtained from a Si(100) surface covered with well defined amounts of Zn. Inset: Difference between the photoemission spectra obtained from Zn clusters on Si(100) and the photoemission spectrum of bare Si(100).

transient signals from 0.15 ML and 0.2 ML Zn on Si(100) obtained by monitoring the Zn 3d photoemission peak as a function of the pump-probe time delay. The transient signals clearly demonstrate that electrons excited in the Si substrate by an infrared pump laser pulse migrate into the Zn clusters, which become negatively charged. The relaxation time constant of the excited electrons in Zn clusters increases dramatically with cluster size from 1.6 ps for 0.15 ML Zn to 26 ps for 0.2 ML Zn. The trapping of the electrons in the Zn clusters is attributed to a Schottky barrier that is formed at the interface between Zn and p-Si(100), which facilitates the separation of electrons and holes after the pump pulse excitation and prevents the hole flow from the p-Si(100) surface to the metal cluster [2]. No electron trapping at small non-metallic Zn clusters is observed. This is attributed to the occupied electronic states of the small

Figure 2. Ultrafast charge carrier dynamics at the surface of a p-Si(100) surface decorated with Zn clusters. (a) Transients obtained from 0.15 ML Zn/Si(100) (squares) and 0.2 ML Zn/Si(100) (circles) by monitoring the shift of the Zn 3d photoemission peak as a function of the pump (800 nm) - probe (23rd harmonic) time delay. (b) Schematic energy level diagram illustrating the band alignment of a Zn cluster on p-Si(100). The red and blue vertical arrows represent the IR-pump and XUV-probe laser pulses, respectively. The dashed curved arrow represent the trajectory of the electron after the photoexcitation of the p-Si(100) surface.

Zn clusters (cf. Inset in Figure 1), located below the valence band maximum of the p-Si(100) surface, which do not lead to the formation of a Schottky barrier between the non-metal cluster and the surface. These experiments clearly demonstrate the ability of the technique to monitor the charge carrier dynamics in nanostructured photocatalytic materials.

Acknowledgements

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