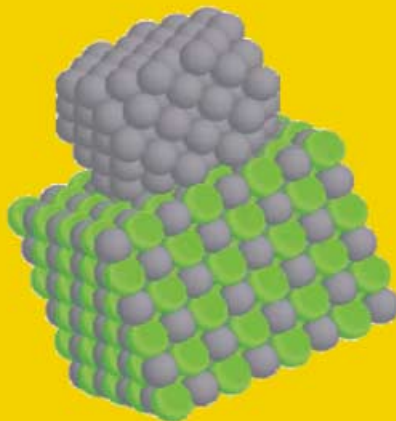
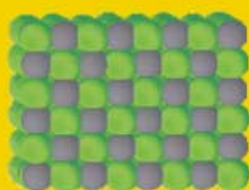
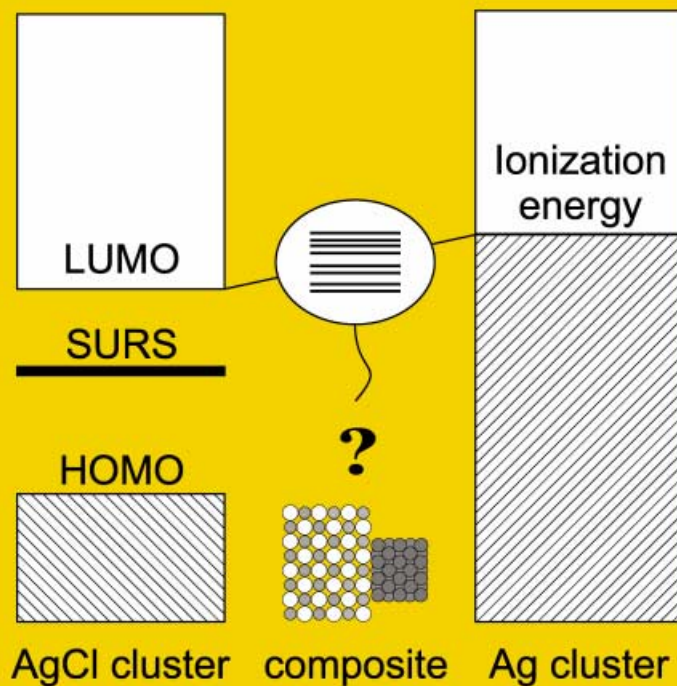


Metal-induced gap states



For more information see the following pages.

What happens at the interface, in terms of electronic states and charge distribution, when a semiconductor and a metal cluster are brought into contact?

Electronic Properties of the Silver–Silver Chloride Cluster Interface

Stephan Glaus,^[a] Gion Calzaferri,^{*[a]} and Roald Hoffmann^{*[b]}

Abstract: The objective of this study was to gain insight into the electronic structure of silver–silver chloride cluster composites and especially into the metal–semiconductor interface. For this purpose a theoretical study of $(\text{AgCl})_n$ ($n=4, 32, 108, 192,$ and 256), of Ag_m ($m=1-9, 30, 115, 276,$ and 409), and of the cluster composites $\text{Ag}_{115}-(\text{AgCl})_{192}$ and $\text{Ag}_{409}-(\text{AgCl})_{192}$ has been carried out. Density of levels (DOL), local density of levels (*l*-DOL), and projection of surface states, as well as projection of properties of individual atoms or groups of atoms obtained in molecular orbital calculations, are shown to be powerful tools for gaining deep insight into the properties of these large systems. The $\text{Ag}_{115}-(\text{AgCl})_{192}$ aggregate, consisting of a cubic Ag_{115} cluster without corner atoms on top of a cubic

$(\text{AgCl})_{192}$ cluster, was found to be remarkably stable with a cluster-to-cluster distance of about 280 pm, and a geometry in which the number of bonding interactions between the silver atoms of Ag_{115} and the chloride ions of $(\text{AgCl})_{192}$ is at its maximum. A sharp jump in charge distribution occurs at the $\text{Ag}_{115}-(\text{AgCl})_{192}$ composite interface. The first AgCl slab picks up negative charge from the two adjacent silver slabs, so that in total the silver cluster is positively charged. In addition, the core of the silver cluster is positively charged with respect to its outermost layer. The main reason for the charge transfer from the

silver cluster to the silver chloride is the newly formed MIGS (metal induced gap states) in the energy-gap range of the silver chloride and the MIDs (metal induced d states) in the d-orbital region. Their wave functions mix with orbitals of the silver cluster and with both the orbitals of the silver and the chloride ions of the silver chloride. The MIGS and the MIDs are of a quite localized nature. In them, nearest neighbor interactions dominate, with the exception of close-lying silver chloride surface states—which mix in to a large extent. We conclude that especially the MIGS not only influence the photochemical properties of silver chloride, but that their existence might be probed by appropriate spectroscopic measurements.

Keywords: cluster compounds • interfaces • nanostructures • silver • silver chloride

Introduction

Metal–semiconductor contacts have been the subject of various investigations for over 100 years. Their behavior led to the discovery of Schottky and Ohmic contacts and to the concept of band bending, illustrated in Figure 1.^[1–4] In the simple Schottky theory, the contact type depends on the relative energy position of the semiconductor band gap with respect to the metal work function. The bending of the conduction and valence band is due to a change in the electrical potential, $-e\phi$, which is caused by electron transfer at the interface region.

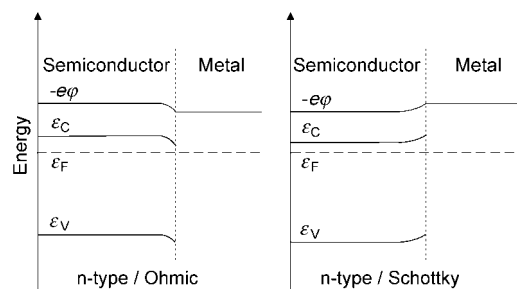


Figure 1. Band representation of an n-type semiconductor in contact with a metal, showing how metals with low work functions lead to Ohmic contacts and metals with high work functions form Schottky contacts. $-e\phi$, ϵ_C , ϵ_F , and ϵ_V represent the electrical potential, the conduction band energy, the Fermi level, and the valence band energy, respectively.^[3]

Microscopic and atomistic cluster aspects are missing in Figure 1. What does happen at the interface, in terms of electronic states and charge distribution, when two clusters are brought into contact, as shown schematically in Figure 2?

Large single-crystal or dense AgCl materials are only slightly light sensitive. Pronounced light sensitivity is observed

[a] Prof. G. Calzaferri, Dipl.-Chem. S. Glaus
Department of Chemistry and Biochemistry
University of Bern, Freiestrasse 3, 3012 Bern (Switzerland)
Fax: (+41) 31-6313994
E-mail: gion.calzaferri@iac.unibe.ch

[b] Prof. R. Hoffmann
Department of Chemistry and Chemical Biology
Cornell University, Baker Laboratory, Ithaca, NY, 14853-1301 (USA)
Fax: (+1) 607-255-5707
E-mail: rh34@cornell.edu