

Computational Study of Sulfur Sensitizing Centers on AgBr

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Abstract

The structure and properties of several possible models for sulfur sensitizers on the AgBr (100) surface has been calculated by the embedded cluster method using density functional theory. The molecule Ag_2S is found to be unable to trap electrons, but Ag_4S_2 can trap electrons if located near a surface kink. This center has a calculated trap depth of several tenths of an electron volt and a long-wavelength singlet absorption, both of which are consistent with experimental data reported for sensitized surfaces. Substitutional dimeric sulfide units incorporated into the surface and compensated by interstitial silver ions were not found to be electron traps. Holes could be trapped on this center and shared equally between the two sulfide ions. It was found that when sulfide is present at a positive kink and compensated by an interstitial silver ion that there is a deepening of the electron trap depth by approximately 0.2 eV. Caused by ion relaxation. These and related centers have been treated and their properties will be compared.

Introduction

The use of sulfur sensitization is well known in high-speed photography. Yet, while several proposals have been offered, the precise structure and workings of the active center remain largely unknown. We approach this problem through the use of computational methods where we extend earlier work.¹ Here we can precisely define the structure of the center for which properties are computed and attempt to correlate these results with various experiments. Photographic and physical studies²⁻⁶ have given evidence that dimers of Ag_2S are active sensitizing centers. Measurements^{4,5,7} have indicated an electron trapping property of the sulfur sensitizing centers with a depth in the range of 0.3–0.4 eV. There is also evidence^{5,6} for hole trapping at some concentration ranges in the formation of sensitizing centers.

Method

This study has employed embedded clusters and is similar to earlier studies on silver halide surfaces.^{1,8} The calculation

is broken into two stages. In the first stage a quantum mechanical calculation using the density functional method is performed for a cluster containing several silver and bromide ions attached to the flat surface comprised of a hemispherical point-ion array and containing approximately 3000 point charges positioned at AgBr lattice sites, such that the entire unit possesses charge neutrality. Then a desired unit of silver sulfide is added to the cluster or substituted for a part of the cluster and its structure permitted to relax to achieve the lowest energy. A second calculation is performed in order to determine the polarization of the silver bromide in response to the silver sulfide unit. The ions previously treated quantum mechanically are fixed at their optimized geometry and represented by shell-model ions having net charge determined by the Mulliken population. This representation of the quantum cluster is allowed to interact classically with the silver bromide ions through Coulombic and short-range potentials. The change in energy upon relaxing shell-model ions representing the AgBr surface from their initial perfect lattice position to their final equilibrium positions is computed and added to the quantum mechanical energy determined in the first calculation. This total energy corresponds to a particular charge state of the silver sulfide. Ionization potentials (IP) or electron affinities (EA) are calculated by energy difference of the appropriate charge states and represent equilibrium conditions because the lattice is fully relaxed.

Results

Ag_2S and Ag_4S_2 Adsorbed to Surfaces

Molecules of Ag_2S and Ag_4S_2 were first studied adsorbed to the flat (001) AgBr surface. The planar quantum mechanical Ag_9Br_8 model is used to represent the (001) surface. These quantum mechanical ions were held fixed and the molecule is allowed to find its low energy position by moving laterally or vertically on the surface. The equilibrium structures calculated for the planar Ag_2S and Ag_4S_2 isomer has its atoms adsorbed almost on top of the underlying surface ions of opposite charge. For adsorbed Ag_2S , neither the filled or empty energy levels fall within the band gap of AgBr. The Ag_4S_2 molecule has a filled level that is 1.0 eV above the conduction band edge so it can trap photoholes.

The electron accepting level is 0.2 eV above the conduction band edge and is not expected to be able to trap photoelectrons.

Defect sites on the flat (001) surface provide an opportunity for stronger interaction of the adsorbed molecule with the surface. Defects consisting of ledges or kinks exist on ionic surfaces and double kinks are thought to be predominant because of their overall long-range zero charge. We employ a quantum mechanical Ag_7Br_7 model embedded within point-ions in order to represent this site. This double kink model has been discussed before^{1,8} in the context of possible sites for latent image growth. It is also a site favorable for adsorption of Ag_4S_2 or Ag_2S . Figure 1 sketches the equilibrium position calculated for the Ag_4S_2 molecule initially adsorbed near this site. The adsorbed molecule is nearly planar and occupies positions with its atoms closest to lattice ions of opposite charge. The properties calculated for the adsorbed molecules at the double kink site are quite different than at the (001) surface site. For Ag_2S no electron trapping is predicted, but the hole trap depth is predicted to be 0.2 eV. In the case of Ag_4S_2 , the data indicates either electron trapping at a depth of 0.3–0.7 eV or hole trapping at a depth of 0.2–0.7 eV is possible. This is the first adsorbed molecule that we have found to be able to trap electrons.

The adsorbed Ag_4S_2 molecule may start to become incorporated into the surface by the addition of crystal ions if they are available in the environment. In this case, one Ag_2S part of the molecule was built into the crystal while the rest of the molecule remains adsorbed to the surface. This type of structure may result from the addition of bromide ions and silver ions near the adsorbed Ag_4S_2 molecule and is sketched in Fig. 1b. The calculation for this case shows a trap depth varying from 0.07 to 0.46 eV for electrons, but an inability to trap holes. It is possible that such a partially incorporated Ag_4S_2 molecule is a S sensitization site. Note that Fig. 1b shows that incorporation in this manner generates a defect site that is a positive kink at the protruding end of the molecule. This site is particularly efficient for latent image growth as earlier calculations^{1,8} have shown.

Substitutional Sulfide at (001) Surface Compensated by Interstitial Silver Ions

Consider the substitution of sulfide for bromide within the top plane of ions on a (001) AgBr surface. In this case, it is necessary to compensate the defect because a double negative sulfide has been substituted for the bromide ion. Interstitial silver ions have been considered to be able to perform this function because of their relatively high concentration near the AgBr surface and high mobility. Thus, we examine this defect for single sulfide and two sulfide ions on adjacent bromide sites. We examine the three different surface clusters shown in Fig. 2. Models (a) and (c) contains a single isolated sulfide and one interstitial silver ion. Model (b) contains two adjacent sulfide ions and two interstitial silver ions. A geometry optimization is

performed for the cluster within the point-ion array. We do not find an electron affinity value large enough to trap electrons at this defect, despite the fact that interstitial silver ions are present for compensation. As far as hole trapping is concerned, the small IP values indicate that this reaction is favored. Thus, we consider surface substitutional sulfide ions to be hole traps.

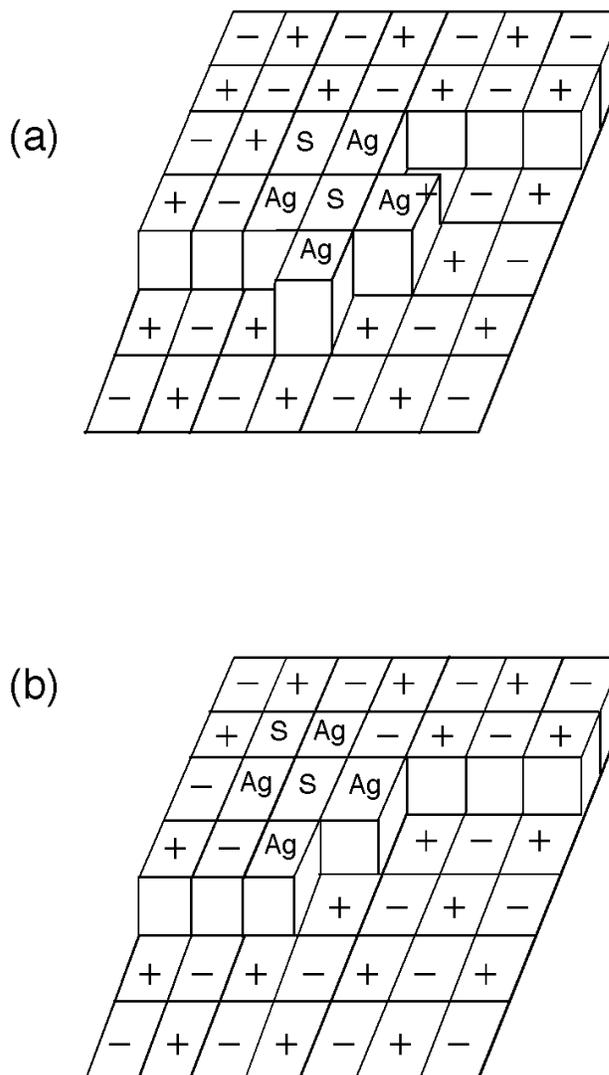


Figure 1. A sketch showing the calculated equilibrium position for Ag_4S_2 near the double kink in (a) and showing in (b) a model representing partial incorporating into the double kink.

Substitutional Sulfide Within a Positive Kink

Positive kinks have been identified by various calculations^{1,8} to be a favorable site on the surface for the growth of photolytic silver. It is possible that during growth of the sensitizing center the sulfide becomes incorporated into a kink. This model corresponds exactly to the incorporation of Ag_2S into the surface defect. In this case, an interstitial silver ion is needed for compensation and would be

expected to be available in the crystal for diffusion to the interstitial site next to the sulfide. The cluster model of a kink was first relaxed, then an electron was added and the change in energy caused by relaxing from the neutral state geometry to equilibrium was calculated. This density functional calculation gave an energy change of -0.24 eV. This relaxation involves displacements of the interstitial silver ion as a major component and is reflective of the electron coupling to the lattice at this kink site. The electron trap depth of an adsorbed silver atom at this site is calculated to be 1.0 eV and thus when an additional electron is trapped, the strong coupling to the lattice will aid the dissipation of energy as the electron falls into the deeper level. In so doing, formation of the silver anion is accomplished that can attract a silver ion interstitial and become converted to the stable Ag_2 and in so doing achieve a nucleation step as in the Hamilton model of strong coupling.⁹

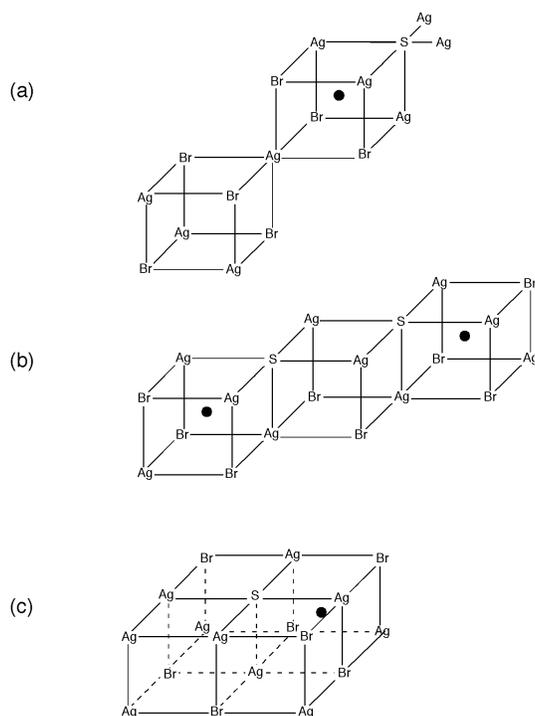


Figure 2. Surface models of embedded quantum clusters representing single sulfide in $\text{Ag}_{10}\text{Br}_7\text{S}$ in (a), disulfide in $\text{Ag}_{12}\text{Br}_8\text{S}_2$ in (b) and single sulfide in $\text{Ag}_{10}\text{Br}_8\text{S}$ in (c). The compensating silver ion is denoted by a heavy dot.

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Biography

Roger Baetzold received his B.S. degree in 1963 from The University of Buffalo and a Ph.D. in 1966 from the University of Rochester. Since 1966 he has worked for Eastman Kodak Company doing experimental and theoretical studies of small metal clusters, catalysts and most recently ionic crystals.