# Photodissolution of Silver in Amorphous $As_2S_3$ Films

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(Received 27 May 1981)

Analysis of published spectral data shows that the photons relevant to photodissolution of metals in amorphous chalcogenide semiconductors are absorbed in the metal and not in the semiconductor. It is argued that light does not enhance the diffusion of metal atoms in the chalcogenide matrix, but triggers a solid-state chemical reaction at the metal-semiconductor interface. A new amorphous phase in the Ag-As-S system, $As_4Ag_5S_6$, is postulated to explain the peculiar physical and chemical properties of the new photogenerated material.

PACS numbers: 61.40.-a, 42.70.Gi

The photographic sensitivity of a thin amorphous chalcogenide film such as $As_2S_3$, deposited on metallic silver, has been discovered by Kostyshin, Mikhailovskaya, and Romanenko in 1965.[1] Since then, the process has been applied to hologram recording, relief image recording, and electrophotography.[2] The process was termed "photodoping," "photodissolution," or "photoenhanced diffusion of metals," and has been found in a wide class of amorphous chalcogenide semiconductor films. Recently this process has been proposed for submicron photolithography, x-ray lithography, and electron-beam lithography in the microfabrication of integrated circuits.[3,4] Despite the obvious technological importance of this process no real progress has been made in the understanding of its mechanism.

Street and Mott[5] proposed the charged trapping centers ($D^+D^-$) model to explain the results of photoluminescence and of ESR measurements in amorphous chalcogenides. This model was further developed by Kastner, Adler, and Fritzsche[6] who interpreted it in terms of bonding configurations unique to lone-pair semiconductors (the valence alternation pairs model). They proposed that the photoenhanced diffusion of silver in amorphous chalcogenide semiconductors may be the result of photoinduced creation of an excess concentration of valence alternation pairs. On the basis of these models and of the results of photovoltage measurements, Ishikawa[7] proposed a mechanism for the photoenhanced diffusion of silver in amorphous chalcogenide semiconductors, according to which the light deionizes the charged centers ($D^++D^-+h\nu\rightarrow 2D^0$), then the metastable $D^0$ states trap electrons released by the silver, and thus an ionized $Ag^+$ front is formed, which is pulled by the $D^-$ states into the chalcogenide semiconductor. This model explains a few experimental observations including the fact that the front of the photodissolved silver in the chalcogenide was observed to propagate with a steplike profile,[8] rather than according to the known solution of the diffusion equation.

Despite this model, the following experimental observations remain unexplained:

(1) What makes the photodoped amorphous chalcogenide such an excellent chemical etch resistant?[2-4]

(2) Inoue, Kokado, and Shimizu reported that the photodoped Ag did not migrate by further exposure to light when there was no (metallic) Ag layer in contact with the chalcogenide glass. If the photodissolved front is pulled into the chalcogenide from the front (e.g., by an internal electric field or by defect-state attraction) the process should continue irrespective of the amount of undissolved silver left behind.

(3) Kolwicz and Chang[4] established that when a layer of metallic Ag, 200 Å thick, sandwiched between a 3000-Å $As_2S_3$ film and a glass substrate, is photodissolved in the chalcogenide film, it gives an etch-resistance protection to a layer of 590 ± 30 Å. This is achieved by a short exposure of less than half a minute, and further exposure as long as 10 min does not change the doping depth.

(4) Goldschmidt, Bernstein, and Rudman[8] found by backscattering experiments that for a 300 Å thick silver layer sandwiched between a glass substrate and various thickness $As_2S_3$ films, the free metallic Ag disappears entirely once the photodissolved silver front has propagated 860 Å in the chalcogenide film. One must appreciate that the difference in the ratio of Ag/photodoped-$As_2S_3$ in the two different experiments 4 and 3 mentioned above is less than 3%.

(5) Calculating atomic ratios, one finds that in experiment 4 the atomic concentration of the photodissolved silver was (32 ± 2)%, giving the

compositional ratio $As_2S_3Ag_{2.4\pm0.1}$. A maximum solubility of a similar order of magnitude was also obtained by others.[10] That large amount of photodissolved silver did not produce any crystalline feature or any significant change in the radial distribution function of the amorphous $As_2S_3$ which is detectable by transmission electron microscopy or by x-ray diffraction to give a clue as to where the silver has disappeared,[10] or whether any new phase has been formed. Furthermore, the $D^+D^-$ model suggests only $10^{17}$–$10^{18}$ states per $cm^3$, which cannot account for a concentration of $1.5\times10^{22}$ silver atoms per $cm^3$ which is obtained by photodissolution.

(6) The photodissolved front was found to propagate in the material with a square-root time dependence.[9,11] This was accepted by many as an indication for a diffusion-controlled process. Yet Goldschmidt and Rudman[12] observed that besides a short induction period at the beginning of the photodissolution, the silver dissolves first linearly with exposure time and towards the end of the photodissolution of the silver the rate slightly decreases. These observed time dependences[9,12] do not seem to agree with each other nor are they in accord with the observed step profile of the propagating photodissolved silver front.[8,13]

(7) The spectral sensitivity of the photodissolution process in various amorphous chalcogenide semiconductor compositions has been measured by many.[1,2,8-10,12] All confirmed the results as first stated by Kostyshin, namely, the photoenhanced transformations begin at an incident photon energy close to or greater than the forbidden bandwidth of the respective semiconductor glass. Yet the spectral dependence of the quantum efficiency comes out wrong: While the absorption coefficient of amorphous $As_2S_3$ changes between $\lambda = 4600$ and $\lambda = 6328$ Å by 4 orders of magnitude, the photodissolution rate changed by a factor of 15 only.[12] Generally a flat wavelength dependence of the photodissolution rate is observed at photon energies less than the extrapolated optical band gap, despite the continuing decrease in the value of the absorption coefficient in that range by a few orders of magnitude.

(8) Whatever model is chosen, it must account for the fact that photodissolution in $As_2S_3$ is one of the only few phenomena unique to the amorphous phase and is hardly detected in the crystalline phase, if at all.[14]

(9) Finally, the right model has to solve all the points satisfied by previous models, for example, the step profile motion of the photodissolved front.

The aim of this Letter is to resolve this sixteen-year-old puzzle. A simple coherent model is given, which shows that all the data above are consistent and it clarifies other points as well. The technological implications of the solution of this problem will be briefly outlined.

The main point which has been overlooked so far is that the reflectance of a metallic layer covered by a (semi-infinite) layer of a semiconductor is given by

$$R_{sm} = \left| \frac{(n_s - n_m) - i(k_s - k_m)}{(n_s + n_m) - i(k_s + k_m)} \right|^2, \qquad (1)$$

where $R_{sm}$ is the reflectance of the semiconductor-metal interface and $n_s$, $n_m$, $k_s$, and $k_m$ are the refractive indexes and the extinction coefficents of the semiconductor and the metal, respectively. $k$ is defined by $k = [\alpha(\lambda)\cdot\lambda]/4\pi$, where $\alpha(\lambda)$ is the absorption coefficient of the specified medium at wavelength $\lambda$ and $\lambda$ is the wavelength in vacuum. Equation (1) suggests the following simple but interesting feature: For a high-reflectance metal like silver, $k_m$ is of the order of 3 throughout the visible, but for a semiconductor like $As_2S_3$, $k_s$ changes over the visible range by some 6 orders of magnitude, from $10^{-6}$ in the red to 0.4 in the blue. As a result, $R_{sm}$ drops from its high value above the semiconductor optical band-gap wavelength to some moderate value below the band-gap wavelength. For $As_2S_3$ on silver this change is from $R_{sm}(\lambda = 5500\ \text{Å}) = 0.968$ to $R_{sm}(\lambda = 4500\ \text{Å}) = 0.468$. If we assume now that the photoexcitation in the photodissolution process takes place entirely inside the metal side of the junction, all the above experimental observations become clear.

(a) If the photoexcitation takes place only in the metallic silver, once the metallic silver has been consumed no further propagation of the photodoped front will be observed.

(b) The photodissolved phase has a step profile because it is pushed from behind; it is not diffusing at all. Its driving force is in the metallic silver. The thermal diffusion of silver in $As_2S_3$ is probably quite low (relative to the propagation spead of the photodissolved front), and "photodiffusion" probably does not occur at all!

(c) The correct spectral dependence of the initial photodissolution rate when the light comes from the semiconductor side is

$$dN/dt = I_0(1 - R_0)\eta[1 - R_{sm}(\lambda)]\exp(-\alpha_s d_s), \qquad (2)$$

where $dN/dt$ is the number of photodissolved silver atoms per unit time, $I_0$ is the incident light intensity in photons/cm$^2$·sec, $R_0$ is the reflectance of the air-semiconductor interface (we neglect multiple reflections for clarity—for values of $\alpha_s d_s$ such that $\alpha_s d_s \leq 1$, formula 2 should be modified accordingly); $\eta$ is the quantum efficiency; $R_{sm}$ is given by Eq. (1); $\alpha_s$ is the semiconductor absorption coefficient; and $d_s$ is the semiconductor thickness (the distance the light has to travel until it reaches the silver). We assume that each photon passing into the silver side is absorbed there,[15] but only a fraction $\eta$ is absorbed close enough to the semiconductor boundary to produce a photodissolution excitation. For values of $d_s$ of the order of $\lesssim 1000$ Å, with $\alpha_s \leq 5\times10^4$ cm$^{-1}$, the main wavelength dependence comes from the term $[1-R_{sm}(\lambda)]$, which gives the factor of 15 mentioned in point 7 above.

(d) Regarding the time dependence of the photodissolution, some raw data had been misinterpreted. If the silver-chalcogenide sandwich is illuminated from the semiconductor side, then, since the region where the silver has already been dissolved has a higher absorption coefficient than that of pure $As_2S_3$,[16] the light reaching the metallic silver layer is attenuated by the new photodissolved phase. With the assumption of linear dependence of the process on light intensity[12] the kinetics equation governing the photodissolution is

$$dX/dt = CI_0(1-R_0)\eta[1-R_{sm}]\exp[-\alpha_s(d_s-X)]\exp(-\alpha_x X), \qquad (3)$$

where $X$ is the width of the photodoped layer, $C$ is a constant converting the number of dissolved atoms to thickness of dissolved layer, and $\alpha_x$ is the absorption coefficient of the new photodoped phase. The solution of Eq. (3) is

$$X = [1/(\Delta\alpha)]\ln(1+\Delta\alpha\cdot At),$$

where $A = CI_0(1-R_0)\eta[1-R_{sm}]\exp[-(\alpha_s d_s)]$ and $\Delta\alpha = (\alpha_x - \alpha_s)$. The function $\ln(1+\Delta\alpha\cdot At)$ has a linear time dependence when $t \ll (\Delta\alpha A)^{-1}$, and in the range $0.5 \leq \Delta\alpha\cdot At \leq 2$ it looks similar to a $\sqrt{t}$ function. Indeed, Goldschmidt was working with very thin films ($X \lesssim 860$ Å) and Shirakawa *et al.* studied relatively thick films ($X$ up to 5000 Å). Their results, then, are not contradictory but rather complementary. To verify this hypothesis we refitted Goldschmidt's raw data[12] and Shirakawa's raw data[11] to the same single $\ln(1+\Delta\alpha\cdot At)$ curve, obtaining a better least-squares fit than either one of them obtained to the linear or to the $\sqrt{t}$ function, respectively. Once these results fit a function $\ln(1+x)$ they do not imply any diffusion mechanism, and can be explained in accord with the step profile of the photodoped front.

The remaining problems can be settled by one more assumption, which is strongly suggested by circumstantial evidence. Let us assume that the light dissolves the metallic silver which results in a solid-state reaction with the chalcogenide, forming a new glassy phase of the composition $As_2S_3Ag_{2.4\pm0.1}$. This may be a new unknown phase of the molecular form $As_4Ag_5S_6$, or a combination of the three known structures $Ag_3AsS_3$, $AsAgS_2$, and $As_2S_2$. $Ag_3AsS_3$, in the crystalline form, does not dissolve in alkaline solutions, but only in $HNO_3$.[17] $As_2S_3$, on the other hand, dissolves only in alkaline solutions and not in acids. If the new phase $As_4Ag_5S_6$ has the right combination of the chemical properties of these two materials, one can appreciate that a new, etch-resistant material has been formed.

The fact that this structure has not been observed so far by x-ray or transmission electron microscopy implies that the major short-range distances of amorphous $As_2S_3$ have been preserved. This can happen if, for example, the silver takes its place in the direction formerly occupied by any of the lone-pair orbitals, or, as is suggested by the compositional ratio $As_4Ag_5S_6$, each silver atom bridges between two $p$ lone-pair orbitals of the $As_4S_6$ structure. This bridging bond is expected to be a weak bond, yet sufficient to produce new chemical properties. Activation energies of ~0.15 eV measured during the photodissolution process may indicate its dissociation energy.[18] The new $As_4Ag_5S_6$ phase may not appear in crystalline form since it undergoes phase separation to the other known structures ($Ag_3AsS_3$, $AsAgS_2$, and $As_2S_2$) at about 160 °C.[14]

One may ask, now, if the excitation takes place entirely inside the silver metal, what is then unique to the amorphous phase which causes the photodissolution in it, and not in crystalline $As_2S_3$. We believe that thermodynamically, at room temperature, the free energy of the $As_4Ag_5S_6$ glassy phase is lower than that of the $As_2S_3$ glassy phase plus metallic Ag. The light helps to overcome a kinetic barrier which slows this reaction. However, the free energy of the $As_2S_3$ crystalline phase plus metallic Ag is lower than both, so that photodissolution is not observed in the crystalline phase.

From the practical point of view, we believe that the understanding of the photodissolution phenomena of silver in amorphous chalcogenide layers will be a breakthrough on the way to 100-Å lithography.[19] The thermodynamics of various glassy compositions of the system Ag-Ge-Se-As-S should be studied so as to find the optimal composition which will give etch protection without the undercutting and lift-off problems observed so far because of the arbitrary choice of silver/group-V(IV)/chalcogen compositional ratios.

Further kinetics measurements of the photodissolution phenomena should be performed either by the etching technique,[4] or, for real-time measurements, by the method used by Goldschmidt and Rudman.[12] Optical probing of the photodissolution may be inaccurate unless one takes into account the three-layer phase system which is formed in the experiment. Photovoltage measurements are not recommended because the high $RC$ time constant of the sandwich geometry masks the relevant effect.

The author expresses his gratitude to Professor R. Weil for critical reading of the text.

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[15] Equation (2) is a good approximation for the most commonly studied case, e.g., a silver layer of 300–500 Å and chalcogenide layer of about 1000 Å in thickness, respectively. For silver layers of thickness $d_m \lesssim \alpha_m^{-1}$, Eqs. (1) and (2) must be modified.

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