

PHOTODEPOSITION FROM COLLOID SOLS

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Photodeposition (PD) from colloid solutions (sols) is a photon-assisted process by which colloid aggregates and thin films are formed on substrates immersed in sols. PD occurs only in the irradiated zones and therefore ultimate material pattern resolution is governed, in principle, by the size of the colloid particles. Holographic methods proved that a line resolution of $0.35(\mu\text{m})$ can be easily achieved. Two systems were investigated so far with this process by which Se and Cd colloid aggregates and thin films were obtained on various substrates from Se and CdS colloid solutions. In this paper common specific characteristics are compared for the two cases.

1. INTRODUCTION

Photon induced deposition processes using light beams or light images as localizing pointers on substrates have been investigated during the past decade in many works^[1-11], intended for microelectronics^[4-11] and photographic imaging applications^[1-3]. In particular, the photodeposition process (PD) of a-Se^[12] and Cd^[13] films from colloid solutions has been investigated during the past 15 years and several mechanisms elucidated^[14,15,16]. Colloid solutions (sols) and liquid media have been used in the past to confine photochemical reactions^[1,17,18] in optical cells. Furthermore, the colloidal particles have been suggested as structural building blocks in photoadsorptive reactions^[1,19,20]. As a result, various reactions have been implemented in spatially well defined aggregates^[1,21,22,23]. In this paper we describe the photodeposition technique in colloid liquid phases. Specifically the PD of a-Se and Cd systems will be described and their properties compared.

2. EXPERIMENTAL

2.1 Microscopic observations

The procedures for preparing photoactive colloid solutions were described in previous publications^[24,25,13]. It consists basically of chemical synthesis of a metastable aqueous colloid solution in the dark which is either in single element form (unary) in the Se case or a binary compound such as CdS in the Cd system. Such an aqueous sol, usually has a solid content of the colloid phase of about 0.1 - 0.5 mg/cc, while the solvated ionic concentration of the photoprecipitating material is about 10 times larger, i.e. 1 - 5 mg/cc. A basic PD photochemical cell is illustrated in Fig.1. Upon irradiation with appropriate electromagnetic wavelength, this metastable colloid solution

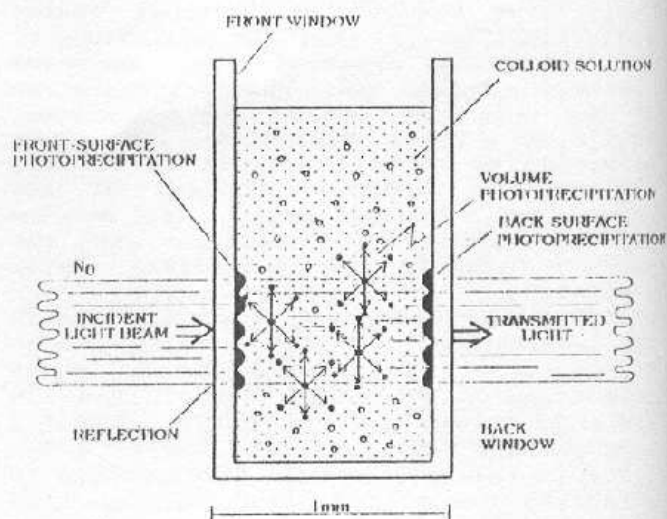
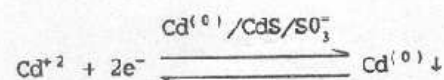
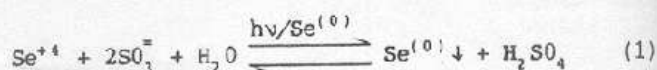


Fig.1 - Schematic representation of a photo-reactor cell used in the investigation of the PD effects for aqueous colloid systems.

favours a redox chemical precipitation which for the two systems investigated, i.e., a-Se and Cd, is given by:



The redox reactions are observed experimentally by a strong precipitation in the form of a "cloud" evolution of very fine colloidal particles of Se or Cd in the bulk of the solution. This effect was termed Volume Photodeposition (VP)^[25]. Another effect which follows and accompanies VP is the so-called Surface Photodeposition (SP)^[26,12] by which Se or Cd particles are first adsorbed in the form of aggregates at any solution discontinuity boundary such as our substrates immersed in it. Then the aggregates grow laterally into bigger colloid particles or merge on the adsorbing surfaces creating thin continuous films^[27], see Fig.2.

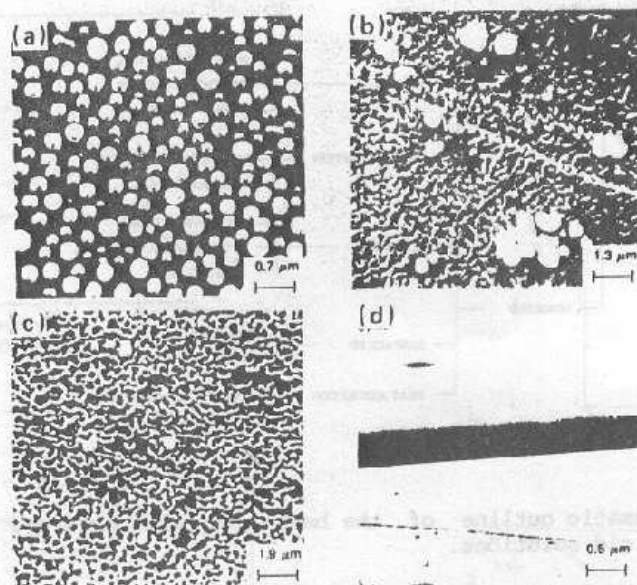


Fig.2 - SEM Micrographs showing several steps in the photoadsorption process during SP on Polymethylmethacrylate (PMMA) substrates:

(a) initial colloid adsorption; (b) and (c) bridging steps of the adsorbed particles; (d) final smooth appearance of the thin film step of a-Se on PMMA substrate.

The SP process takes place at sites where photons encounter solution/substrates interfaces, see Fig.1. The substrates used in PD investigations were transparent materials such as plastics (PMMA, Mylar, Styrene), glass and conductive films such as gold, tin oxide and indium tin oxide. The PD processes were investigated thoroughly at room temperature and in some cases in the whole temperature region of 5 - 40(°C) (1,2,3,13,24,25). The SP kinetic experiments were usually performed in terms of film thickness growth dependence vs. parameters such as: time, light intensity, temperature colloid concentration and wavelength^(1,2,13,28). The VP processes have been investigated to date only to a limited extent^(24,25). However, the basic subprocesses induced by the light irradiation in the colloid solutions have been isolated and they are outlined schematically in Fig.3.

2.2 Basic Kinetics of SP

It is clear from Fig.3 that the overall conversion of photon energy into photo-precipitated and photoadsorbed species is of a very complex nature. In particular, the SP film growth behaves in a nonlinear fashion (see Fig.4) due to light absorption in the growing film or due to material depletion from the colloid solution. If it were possible to maintain

constant light excitation over the whole sequence of the layer growth, some intrinsic law governing the photodeposition effect should become evident. Empirically a logarithmic law, so-called Elovich equation, describes quite well the curves of Fig.4(a).

$$\xi(t) = K \ln \left(1 + \frac{t - \tau_1}{\tau^*} \right) \quad (3)$$

where τ_1 is the incubation time which refers to the period of time needed for a compact layer to be formed on the substrate by the SP process^(1,2). ξ is the film thickness and K and τ^* are constants of the growth equation.

2.3 Light intensity dependence of SP

Using laser sources with high light intensities⁽²⁸⁾, we were able to reduce the incubation period appreciably, to allow real time photodeposition processing, see Fig.5(a), where τ_1 is less than 30 (sec). Moreover, by plotting $\log(\tau)$ vs $\log(I)$, a specific power law could be deduced mathematically for a wide range of light beam excitation intensities I ⁽²⁹⁾:

$$\tau_1 = \tau_{01} \cdot I^{-n}$$

where $\tau_{01} = 56$ and $n \approx 0.6$, see Fig.5(b).

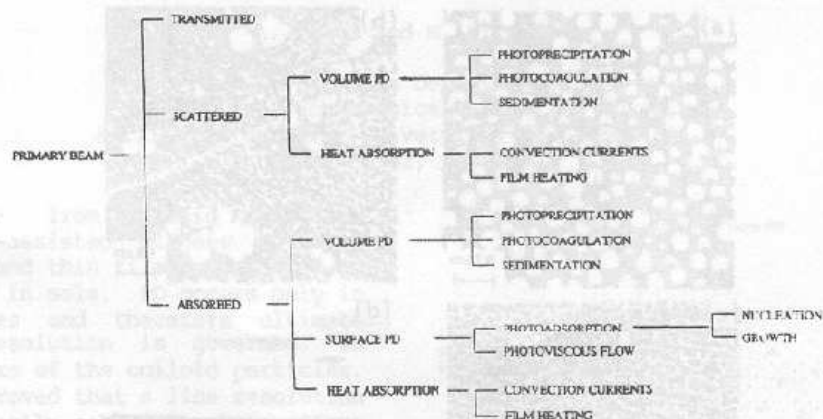


Fig.3 - Schematic outline of the basic processes observed for PD of colloid solutions.

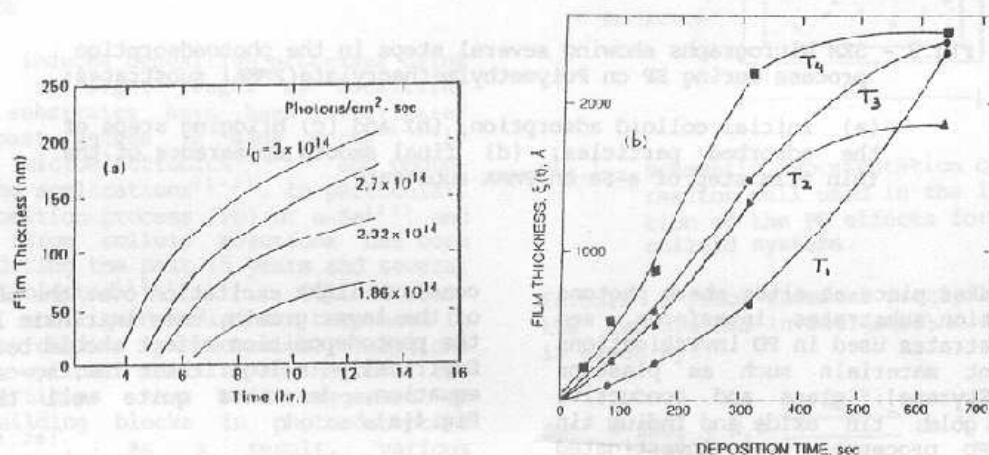


Fig.4 - Film thickness-time relationship:

- (a). for a-Se with light intensity I_0 as parameter; mercury discharge lamp $\lambda = 435(\text{nm})$; $T = 5(^{\circ}\text{C})$; substrate PMMA.
 (b). for Cd with temperature as parameter $T_1 = 0.5^{\circ}\text{C}$, $T_2 = 5^{\circ}\text{C}$, $T_3 = 10^{\circ}\text{C}$, $T_4 = 15^{\circ}\text{C}$; UV fiber source of 2.7 W/cm^2 ; substrate PMMA.

For the low light intensity range, the data were obtained from experiments with incoherent discharge light sources⁽¹¹⁾ while the high intensity points were recorded by using laser sources⁽²⁸⁾.

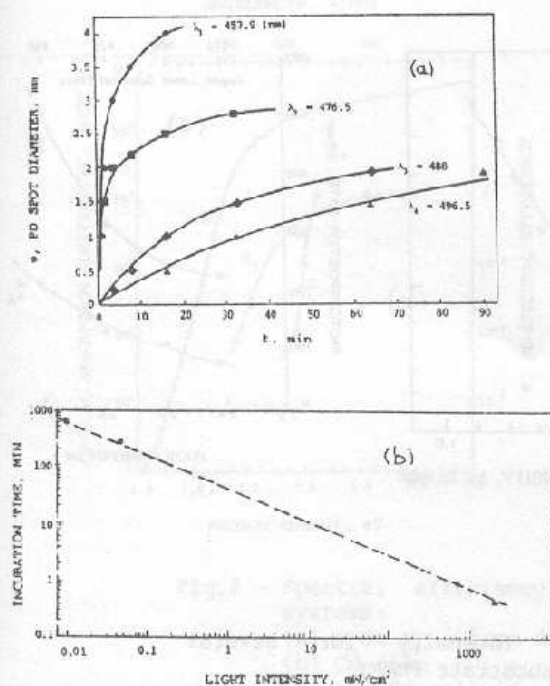
By differentiating Elovich equation (3), one obtains the rate of Surface Photodeposition (SP) in terms of film thickness growth:

$$\frac{d\xi(t)}{dt} = \left(\frac{K}{\tau^*}\right) \exp\left(-\frac{\xi(t) - \xi_1}{K}\right) \quad (5)$$

where K/τ^* is called the Quasi-Linear Deposition Rate (QLDR), and it characterizes the initial slopes of Figs. 4 and 5(a). K was found to be a constant which reflects the light absorption process⁽¹⁵⁾ causing SP. τ^* was identified as the period of time during which the SP process is not hampered strongly by the light absorption in the growing film. Hence it contains the physical information about the SP mechanisms⁽¹⁵⁾.

2.4 Photon-temperature activation of SP

By plotting QLDR vs. $1/T$, we obtained curves of the form given in Fig.6(a). This plot expresses the intrinsic physical behaviour of the



- (a) - $\phi(t)$ - laser photodeposited (a-Se) spot diameter as a function of time and wavelength: $T = 25(^{\circ}\text{C})$; light power $I_0 = 150 \text{ mW}$; Argon Ion Laser; various wavelengths, λ .
- (b) - Log-log plot of the incubation predeposition time period τ_1 vs. light intensity; (a-Se); photon energy $2.65 \pm 0.5 \text{ eV}$; $T = 22(^{\circ}\text{C})$.

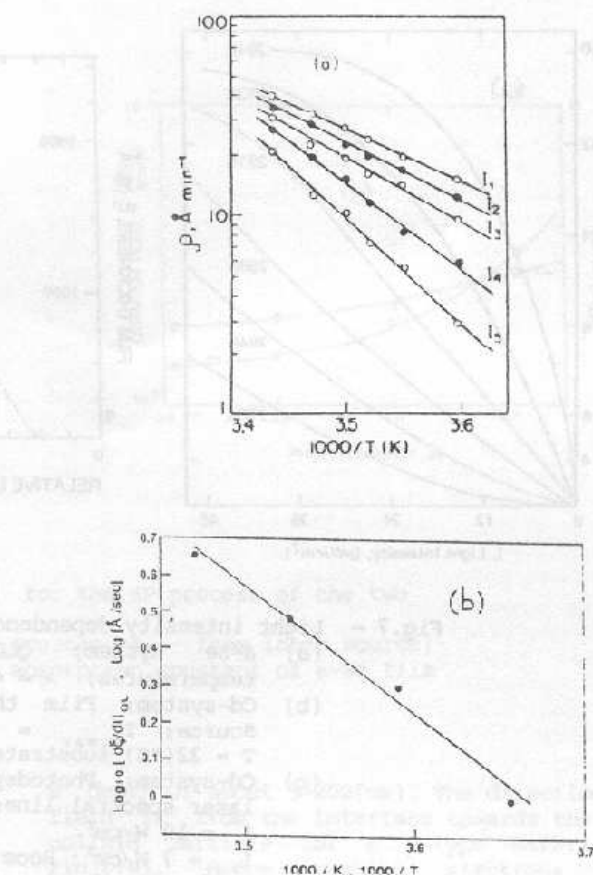


Fig.6(a) - Arrhenius plot for a-Se obtained from Fig.4(a); $I_1 - I_5$, $52 - 25 \mu\text{W}/\text{cm}^2$.

(b) - Arrhenius plot for Cd obtained from Fig.4(b).

SP rate as a function of light intensity and temperature. In fact, from Fig.6(a) one can realize easily what is meant by the statement that SP is both a photon and thermally activated process. The linearity of the QLDR vs. $1/T$ plots in Fig.(6) show that the thermal activation process of the SP can be approximated by an Arrhenius law:

$$\left. \frac{d\phi}{dt} \right|_{t=\tau_1} = \dot{\xi}_0 \exp(-\Delta/kT) \quad (6)$$

where typical activation energies of $\Delta = 0.3 - 1.0 \text{ eV/atom}$ were obtained for a-Se⁽¹⁶⁾ and $\Delta = 0.67 \text{ eV/atom}$ for the Cd system⁽¹³⁾.

The light intensity, I , dependence is empirically of a power law⁽²⁾ type:

$$\dot{\xi} = \dot{\xi}_0 \cdot I^m \quad (7)$$

and the photon energy dependence⁽²⁾ is of an exponential form:

$$\dot{\xi} = \dot{\xi}_0 \exp(-qh\nu/kT) \quad (8)$$

where q is a constant and $h\nu$ is the photon energy. See plots for a-Se and Cd in Fig.7. m for a-Se is in the range $m = 0.5 - 2$, while for the Cd system it has not yet been investigated. q - has not yet been fully investigated even for the a-Se system⁽²⁾.

2.5 Spectral dependence of the SP process

Spectral efficiency curves of the SP process are also important to obtain from the process wavelength or photon energy dependence, due to possible clues for the physical origin and mechanisms involved in PD. The results obtained for the a-Se and Cd systems are shown in Fig.8.

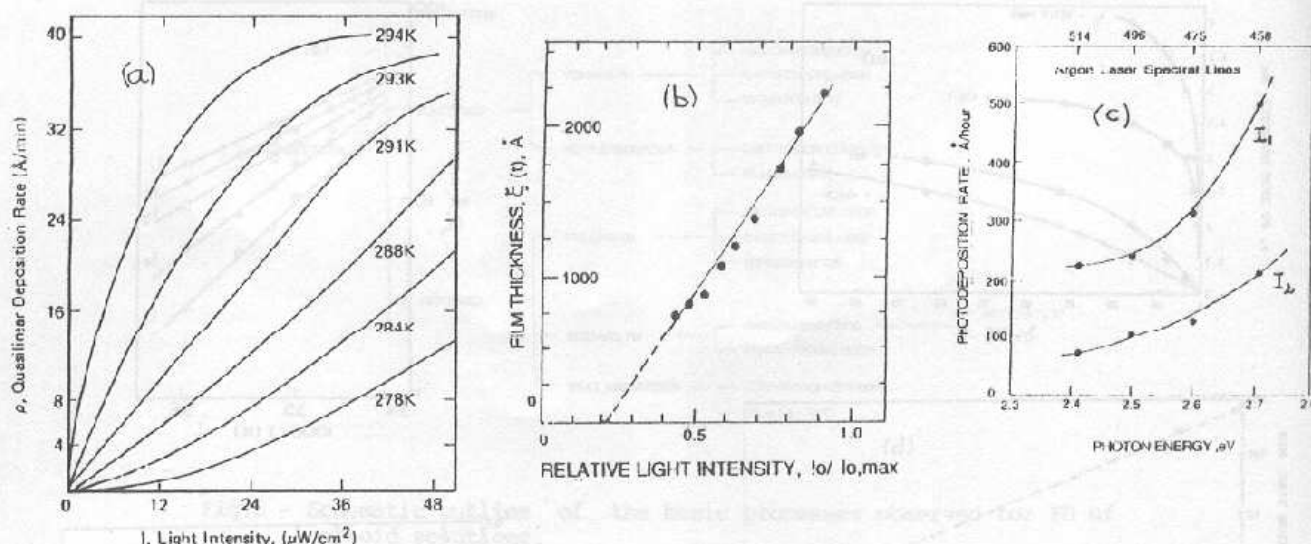


Fig.7 - Light intensity dependence for:

- (a) a-Se system; QLDR vs. Intensity for several temperatures; $\lambda = 435\text{nm}$; substrate PMMA;
- (b) Cd-system; Film thickness vs. Intensity; UV Fiber Source; $I_{0,\text{max}} = 2.7 \text{ W/cm}^2$; Exposure, $t = 640 \text{ sec}$; $T = 22(^{\circ}\text{C})$ substrate PMMA.
- (c) Cd-system; Photodeposition rate as a function of Ar laser spectral lines:
 $I_1 = 10 \text{ W/cm}^2$
 $I_2 = 7 \text{ W/cm}^2$; Room Temperature; PD performed on a thin predeposited layer of Cd by UV source on PMMA substrate.

The spectral efficiency QY_{SP} used in Fig.8 is defined by the equation:

$$QY_{SP} = \frac{M}{I_0 \cdot \tau_d} \quad (9)$$

where I_0 is the constant photon flux entering the colloid system from the light source, M the photodeposited mass and τ_d the period of film photodeposition. For a-Se, QY_{SP} is normalized, where at $h\nu = 3.1(\text{eV})$ the absolute value is about 0.01 atoms/photon.

2.6 Resolution features of the SP process

Using conventional contact masks, projection light methods and coherent laser interference methods^(1,3,12) we were able to obtain pattern resolutions down to $0.35(\mu\text{m})$ linewidth for the a-Se system and about 100 linepairs/mm for the Cd colloid system. The results for the Cd are only preliminary since direct deposition on foreign substrates requires UV light and hence the deposition was performed with metallic masks. A typical resolution test pattern obtained by the SP process is shown in Fig.9:

3. DISCUSSION

Referring to the photochemical reactions (1) and (2), one observes that there is a basic difference between the a-Se and Cd systems. The a-Se system consists of a homogeneous colloid type system where an autocatalytic effect creates new Se precipitated particles. In contrast, the Cd system employs a CdS colloid solution which heterocatalyzes Cd ions precipitation from the solution. However, for both systems the basic kinetics shown in Figs.(4) show a saturation effect at long periods. This points to the overwhelming influence of light absorption in the photogenerated film and also to the basic importance of the light absorbing properties of the photoactive colloid particles. In both systems investigated, the PD is a photon and temperature activated process represented mathematically by equations (6) and (7) see Fig.(6). Light intensity enhances the growing rate in a nonlinear fashion, although the film thickness is linear in light intensity, see equation (7) and Fig.(7). For the Cd system we found an interesting interrelated time, substrate type, and wavelength dependence for the PD process: The aged metastable solution needs UV light, i.e., $\lambda < 350\text{nm}$ to start the VP and SP process. In contrast, the freshly prepared CdS

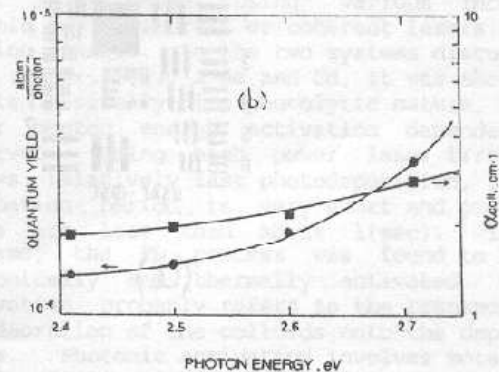
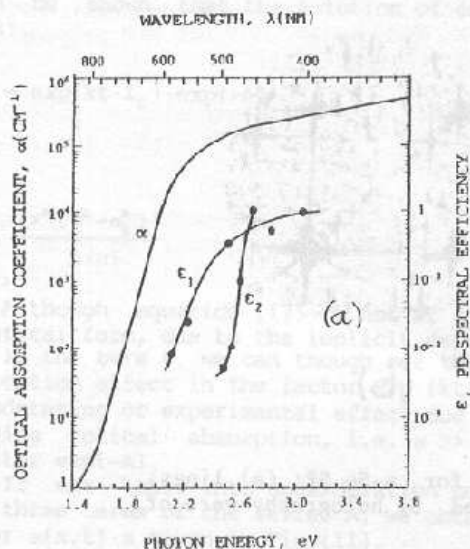


Fig.8 - Spectral efficiency curves for the SP process of the two systems:

(a) a-Se ϵ_1 - from discharge sources, ϵ_2 - from laser source;
(b) Cd-film PD: α - optical absorption constant of a-Se film and Cd colloid.

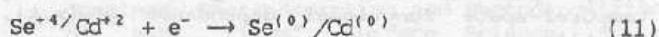
colloid sol is VP photoactive even when irradiated with visible light of $\lambda > 435(\text{nm})$, but the SP is of low quality and irreproducible results are obtained. However, when a substrate with Cd predeposited layer is immersed in the aged sol, and irradiated with Ar laser visible lines, see Fig.7(c), SP proceeds on the surface although no VP is observed in the bulk. Hence, for the Cd system where two different colloids coexist, i.e. CdS and Cd, we have been able to observe⁽¹³⁾ a distinct step of direct photoadsorption on the surface, a feature which could not be deduced from a-Se experiments^(1,2,8).

4. MODELS

4.1 Volume Photodeposition

A tentative mechanism of bulk volume colloid photoprecipitation (VP) in our systems may consist of a two step process. Initially the photoactive colloid a-Se⁽⁰⁾ or CdS⁽⁰⁾ absorbs the photons, thereby generating pairs of electrons and holes in the conduction and valence band respectively^(2,9). To obtain a chemical reaction, some separation of the e⁻h⁺ pairs should occur before recombination and heat conversion occurs. Such a separation can be achieved by external electrical fields or internal pn junction like potential barriers. However, such potential barriers which may assist in the separation of e⁻h⁺ pairs exists naturally in colloid particles, due to the fact that most colloid particles being immersed in a solution are prone to charge transfer at the interface because of the difference of the electrochemical potential of the two phases. The net result is the formation of an electrical field at the colloid surface to

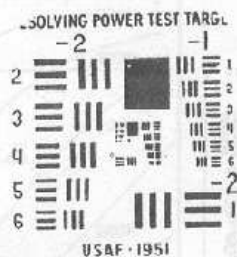
a depth of about 5-200(nm). The direction of the field is from the interface towards the bulk of colloid particle for a p-type material, see fig.(10), hence pushing electrons to the interface and creating conditions for photoreduction. Photoreduction is here the chemical reaction which causes the precipitation of additional a-Se⁽⁰⁾ or Cd⁽⁰⁾ from the Cd⁴⁺ solvated ions:



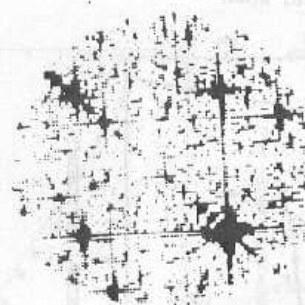
The photogenerated electron in the colloid particle moves to the interface where an acceptor species in solution such as Se⁺⁴ or Cd⁺² can be reduced. The holes, on the other hand, move to the interior of the colloid and are eventually trapped by a counter donor species in the solution, oxidizing it:



This model is of a photoelectrochemical orientation but it contains elements from pn junction theory. We assume in both systems, i.e., a-Se and CdS that the colloid particles have a p-type bulk property. In fact, the a-Se solution system must be acidic to create this condition while the CdS sol must be slightly basic. Hence each colloid is pictured as a "short circuited" photoelectrochemical cell where the pair production of e⁻h⁺ causes redox and oxidation of ionic species in the solution. The redox process, however, is of a catalytic type,



(a)



(b)

Fig.9 - Resolution test patterns obtained for a-Se SP; (a) lines; (b) dots. Best linewidths obtained by holography were of $0.35(\mu\text{m})$.

i.e., we observe that for the a-Se system there is a strong precipitation effect enhanced by the additional precipitation of the newly created colloid particles during photoexcitation. This interesting feature, which may be called an autocatalytic effect for the a-Se colloid particles, has a resemblance to the photographic amplification effect in silver halides. The amplification is understood here in the sense that existing a-Se particles are created by a positive feedback loop of photoprecipitation - photon absorption causing an avalanche process which makes the irradiated zone close to the window very photoactive but also obstructing the light penetration into the bulk of the solution. Mathematically, we can model this acceleration PD effect as follows: Given a colloidal system irradiated with light of intensity I_0 , the photoprecipitation optical effect in the bulk (VP), can be described by the following temporal-space functional dependence $g(\alpha(x,t), I(x,t))$:

$$\frac{d\alpha(x,t)}{dt} = g(\alpha, I) \quad (13)$$

where $\alpha(x,t)$ is the optical absorption coefficient of the colloid sol and $I(x,t)$ the light intensity, both functions being dependent on time and space. In our particular system, the function $g(\alpha, I)$ can be given by the general semi-empirical form:

$$g(\alpha, I) = k \cdot \alpha^e(x,t) \cdot I_0^m(x,t) \cdot e^{-\alpha(x,t) \cdot x \cdot m} \quad (14)$$

where k , α , e , I_0 , m and x are a proportionality constant, optical absorption coefficient of the solution, absorption multiplicity number, incoming light intensity, photon multiplicity number and the distance into the solution respectively. α is dependent on the colloid properties through the relation $\alpha = \sigma \cdot N$ where N is the volume concentration of the colloid particles, and σ is the single particle optical

absorption cross section. From the experimental observations⁽²⁵⁾ we were able to conclude that $e = 1$. To simplify the derivation we will also assume that $m = 1$, simplifying the equation to:

$$\frac{d\alpha(x,t)}{dt} = k \cdot \alpha(x,t) \cdot I_0 \cdot e^{-\alpha(x,t) \cdot x} \quad (15)$$

With the conditions:

$$\alpha(\text{for any } x, t = 0) = \alpha_0 \quad (16)$$

$$I(x = 0, \text{for any } t) = I_0$$

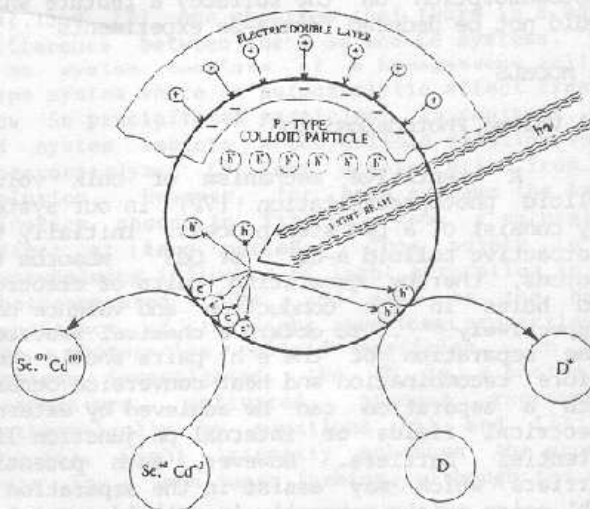


Fig.10 - Schematic model for the photoredox effect in a p-type colloid particle leading to photoprecipitation or photoadsorption.

it can be shown that the solution of equation (15) is:

$$\frac{\alpha(x,t)}{\alpha_0} = \exp(kt \cdot I_0) \cdot \exp(-A) \quad (17)$$

where

$$A = \sum_{n=1}^{\infty} \frac{[x^n (\alpha^n - \alpha_0^n)]}{n \cdot n!} \quad (18)$$

Although equation (17) is not of a simple mathematical form, due to the implicit dependence of α in the term A , we can though see the clean amplification effect in the factor $\exp(ktI_0)$ and the moderating or experimental effect due to the increasing optical absorption, i.e. $\alpha \gg \alpha_0$, in the factor $\exp(-A)$.

If one takes into consideration only the first three terms of the series A , we obtain the plot for $\alpha(x,t) \cdot x$ given in Fig.(11).

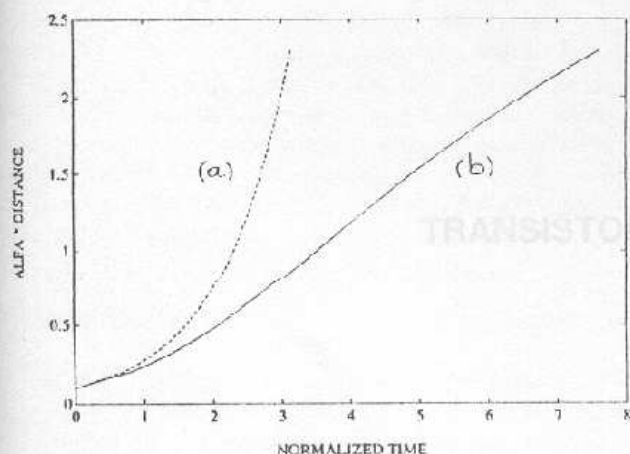


Fig.11 - Plot of $\alpha(x,t) \cdot x$ as a function of the nondimensional time variable $(ktI_0 t)$,
(a) clean effect with $A = 0$;
(b) moderating effect with $A \neq 0$, for $\alpha_0 x = 0.1$

This theoretical result describes qualitatively the experimental forms of $\alpha(x,t)$ obtained during the VP process^(25,14). The question whether a true amplification process also occurs during the surface photoprecipitation, can be resolved if one looks into the spectral photodeposition yield. It seems from up-to-date experiments that since the SP spectral yield is < 1 , there is no amplification or multiplication effect as is the case in the photographic processes of silver halides. This difference as compared to the VP process stems from the fact that SP being a thin film growing process involves rate determining steps such as Brownian transport or adsorption of the depositing particles from the sol to the substrate. Those mechanisms, however, are not of an amplifying character.

5. CONCLUSIONS

The SP process from colloid solutions has been investigated using various incoherent visible and UV sources or coherent lasers such as Ar ion lasers. In the two systems discussed in this paper, i.e., a-Se and Cd, it was shown that SP is basically of a photolytic nature, since a clear photon energy activation dependence is observed. Using high power laser irradiation allows relatively fast photodeposition, i.e. the incubation period is very short and processing times are less than about 1(sec). In both systems, the PD process was found to be both photonically and thermally activated. Thermal activation probably refers to the transport step or adsorption of the colloids onto the deposition sites. Photonic activation involves more subtle photoexcitation mechanisms. Holographic methods were used to realize pattern resolution features of about 0.35(μ m) linewidth. Being a material direct writing process, SP may be of potential use in microelectronics, optronics and new image recording technologies.

6. ACKNOWLEDGEMENT

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