

SPRAY PYROLYSIS PROCESSING

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INTRODUCTION

Spray pyrolysis is a process in which a thin film is deposited by spraying a solution on a heated surface, where the constituents react to form a chemical compound. The chemical reactants are selected such that the products other than the desired compound are volatile at the temperature of deposition. The process is particularly useful for the deposition of oxides and has long been a production method for applying a transparent electrical conductor of SnO_x to glass (1). There have been many studies in this area since the pioneering paper by Chamberlin & Skarman (2) on CdS films for solar cells (3, 4) in 1966, among them a review of transparent conductors (5) and a bibliography Pamplin (6) presented at a conference on spray pyrolysis. We discuss here the method and its control; the properties of the films that have been deposited (particularly in relation to the conditions); some specific films, particularly CdS; and device application.

THE DEPOSITION PROCESS

Viguié & Spitz (7) classified chemical spray deposition processes according to the type of reaction. In process A, the droplet resides on the surface as the solvent evaporates, leaving behind a solid that may further react in the dry state. In process B, the solvent evaporates before the droplet reaches the surface and the dry solid impinges on the surface, where decomposition occurs. In process C, the solvent vaporizes as the droplet approaches the substrate; the solid then melts and vaporizes, and the vapor diffuses to the substrate, there to undergo a heterogeneous reaction. (They identify this process as true chemical vapor deposition.) In process D, the entire reaction takes place in the vapor state.

In all processes, the significant variables are the ambient temperature,

carrier gas flow rate, nozzle-to-substrate distance, droplet radius, solution concentration, solution flow rate, and—for continuous processes—substrate motion. To this list one should add the chemical composition of the carrier gas and/or environment, and, most importantly, substrate temperature. Most spray pyrolysis depositions are type A or B, and our discussion centers on them.

Figure 1 shows a typical spraying system. It provides for flow measurement of both the propellant gas and the liquid. With spraying areas of a few square centimeters, liquid flows of 1–20 ml/min have been reported. Sufficiently low-flow commercial pneumatic spray heads are not readily available, and a needle valve is needed to restrict the flow. Acidic solutions attack stainless steel to the extent that iron contamination of the deposit is a problem. A pyrex glass spray head can be used with success (8). Other atomizers, such as a resonant cavity or a piezoelectric transducer, can be used. The substrate heater is a metal block, a liquid metal bath with a

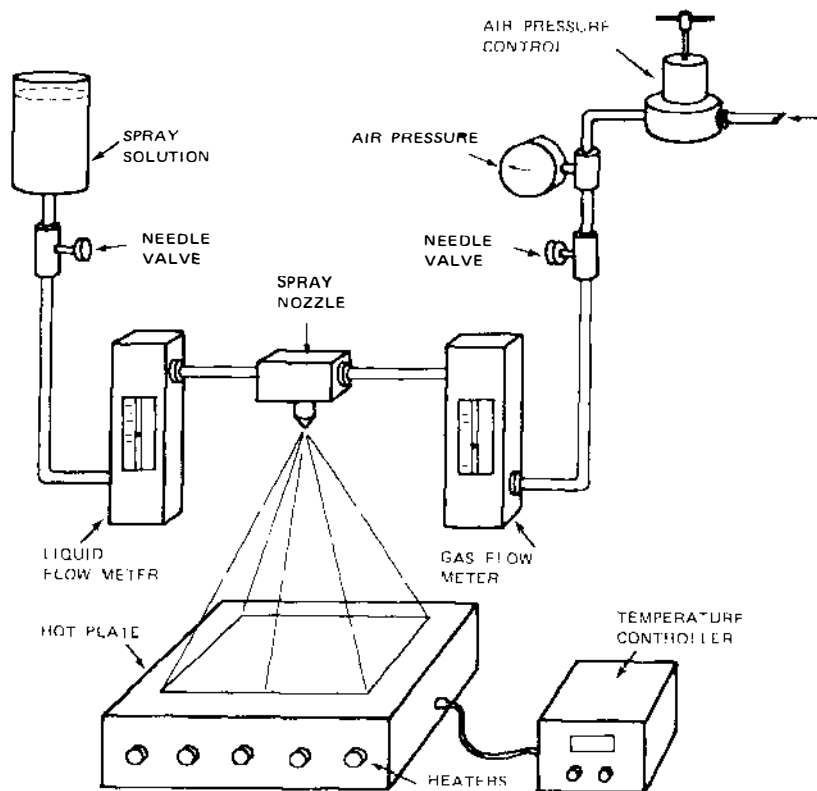


Figure 1 Spray pyrolysis system.

thermocouple, and a controller, or infrared (IR) lamps. A 1-kW heater is typical. Air is the usual propellant, typically at 20 psi with a flow rate of 20 liters/min. When oxygen contamination is a problem, an inert gas with an enclosure is used. Because spray patterns are inevitable and result in uneven deposition thickness, a random motion of the spray head, the substrate, or both is useful for uniform deposition (8–12).

Surface temperature is a critical factor in spray pyrolysis (13), yet most investigators have not known the actual surface temperature. The surface temperature as measured (8) by an infrared pyrometer is about 50°C less than the temperature of the tin bath. Lampkin (14) determined that the sheet resistance of a transparent conductor affects the rate of growth of a CdS film being deposited on that surface. (We interpret a similar observation as being due to the difference in infrared emissivity of the conductive surface compared to the bare glass.) The emissivity of a conductive SnO₂ surface is about 10% (15). Because deposition efficiency decreases as temperature increases above a critical value, we conclude that the efficiency of deposition is reduced because the surface temperature of the transparent conductor is actually higher than that of a bare glass surface at the same substrate heater temperature under the same flow of air and liquid.

Various methods have been used to control surface temperature. Liquid metal baths provide better thermal contact than does the most perfect solid surface, because the wetted interface is in contact everywhere while solid surfaces are actually in contact with less than 1% of the surface area. Radiant heat has been used to avoid the problems associated with liquid metals in contact with corrosive vapors (12). Spraying in pulses or bursts, which has been used to assure that the surface temperature is reasonably constant (16–18), can be conveniently combined with spray head and substrate motion, which also contributes to uniform deposition (Mooney-Brodie, patent applied for). Other investigators have gone to great lengths to hold the temperature constant to within $\pm 5^\circ\text{C}$ (9, 19). Fahrenbruch (private communication) suggested that a surface thermocouple prepared by vapor deposition of a bimetal, such as Rh–Rh + 1% Pd, would provide a measure of the temperature of a glass surface during deposition. This is a worthy suggestion, but it might be hindered by the emissivity problem discussed earlier.

The atomization process is another critical factor in spray deposition. Process A, in which the droplet lands and reacts and the solvent evaporates, is the mechanism of most spray pyrolysis processes, and conditions that result in the maximum number of droplets having the size and momentum to land and flatten are critical. A great deal of work has been reported on a wide variety of compounds, but very little has been published on the process

itself and the importance and control of process variables. Lampkin (20) studied the dynamics of the spray process. Stroboscopic photography of the impinging droplets showed that, depending on its velocity and flow direction, a droplet will either flatten, skip along the surface, or hover motionless. Lampkin concluded that droplet size and momentum are the important variables. He also studied the spray envelope, the entrainment of ambient air, and the effect of an electric field applied between the spray nozzle and the substrate.

Concentration of the spray solution ranging from 0.1 to 0.001 M is another critical variable. Very smooth CdS surfaces are obtained at low flow rates using acetate solutions (Mooney-Brodie, patent applied for). Very smooth surfaces with columnar grains have been produced from chloride solutions (20), as have rough deposits showing a serpentine pattern with small grains forming hollow nodules (21, 22). Although experimental details that explain the differences between the widely different surfaces produced by the same laboratory are not given, smooth films of columnar grains are obtained with low concentration and low solution flow rates (to be published).

Grain size is small for spray-pyrolyzed films, usually less than $0.5\ \mu\text{m}$ in cross section (22). Viguié & Spitz (7) showed a photomicrograph of a deposit representative of processes A and B. The circular pattern has a diameter of $75\ \mu\text{m}$. The drop flattens when it lands, so its diameter was probably about $20\ \mu\text{m}$ and its volume was about $4 \times 10^{-9}\ \text{cm}^3$. If this deposit was CdS deposited from a 0.1-M solution of CdCl_2 and $(\text{NH}_2)_2\text{CS}$, the mass of the deposit would be $6 \times 10^{-11}\ \text{g}$ and its volume $1 \times 10^{-11}\ \text{cm}^3$. If each grain was a cube $0.5\ \mu\text{m}$ on a side, the volume would be $1.25 \times 10^{-13}\ \text{cm}^3$, and a single drop would represent about 80 grains.

Another factor influencing the mechanism of film growth is the time available for a drop to react before a second drop strikes the same surface. A solution flow about 4 ml/min represents 10^9 drops/min over an area of about $80\ \text{cm}^2$ (22), which is about 2×10^{-6} times the area of the original $75\text{-}\mu\text{m}$ drop pattern. This represents 2×10^3 drops/min striking the same area, or about 33 per second. With 30 ms for reaction and evaporation of the water before the next drop strikes, there is little time for the growth of crystals.

Films that are grown very slowly and at low temperature, such as from a 0.001-M solution at a flow of 2 ml/min at about 275°C surface temperature for CdS (submitted for publication), may actually grow in an atmosphere saturated in water vapor or possibly form an aqueous film that resides on the surface. This slow growth results in columnar grains oriented roughly perpendicular to the substrate surface and of about $0.3\text{-}\mu\text{m}$ cross section, extending through the $2\text{-}\mu\text{m}$ film as shown in Figure 2. Because the film is

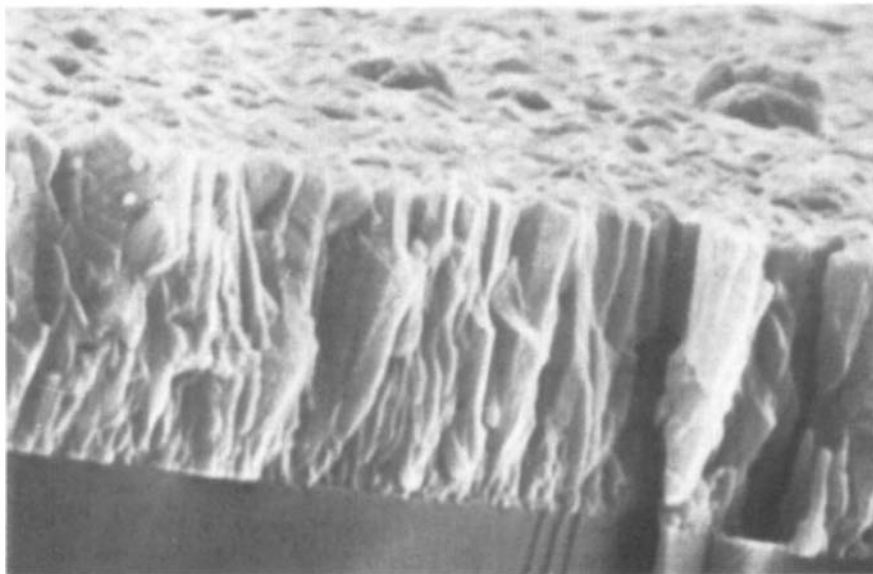


Figure 2 CdS film deposit from 0.001-M solution.

grown over a 2-hour period, the crystallites have to grow without each drop nucleating a new grain. The attraction of spray pyrolysis is primarily its low cost (11, 23), so the use of slow growth rates to obtain films of better morphology may not be practical.

Most spray pyrolysis is done from aqueous solutions. This is conducive to a low-cost process, and spraying flammable liquids on a heated surface can be exciting, if not dangerous. However, some investigators (19, 24) have developed processes using nonaqueous solutions. Viguié & Spitz (7) distinguish their process C as different from conventional spray pyrolysis (processes A and B) because the volatile solvent evaporates before striking the surface, leaving vapors to react at the surface.

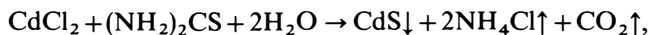
CdS Deposition

The majority of the papers on spray pyrolysis concern CdS, which was the principal compound studied by Chamberlin & Skarman in their first paper (2). Their apparatus was similar to that shown in Figure 1, and they reported a substrate temperature of 320 to 380°C—but how and where it was measured was not stated. The solution flow rate was 15 ml/min and the concentration was 0.01 M. The cadmium source compounds were chloride, acetate, formate, and nitrate. Films sprayed with CdCl₂ were crystalline; acetate solutions produced amorphous deposits. The sulfur sources were thiourea; *N,N*-dimethylthiourea; allylthiourea; thioacetic acid;

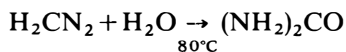
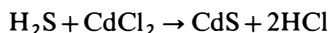
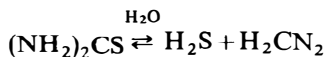
2-thiozoline-2-thiol, and ammonium thiocyanate. The best results were obtained with cadmium chloride and thiourea. Stoichiometry of the solution was assured by precipitating the complex formed by mixing 1-M solutions of CdCl_2 and thiourea and redissolving the precipitate to produce the dilute solutions used for film preparation. The decomposition temperature of the complex, 210°C , was determined by differential thermal analysis; this should be the minimum temperature for film preparation from the chloride, but highly resistive films of CdS for electrophotographic applications have been prepared from acetate solutions at 180°C (Mooney-Brodie, patent applied for).

The CdS films are crystalline, and the intensity of the x-ray diffraction peaks and the degree of preferred orientation depends upon the cation/anion ratio in the spraying solution and the substrate temperature. Postdeposition heat treatment is also important. Crystallinity is strongly influenced by the substrate (25). Films sprayed on ceramics and metals that have crystalline grains on the surface are not very crystalline, while crystalline deposits are obtained on an amorphous substrate (such as on glass). The explanation of this phenomenon is that the crystalline surface affords many nucleation sites and the large number of crystallites compete, while an amorphous surface leads to fewer nuclei that can grow larger.

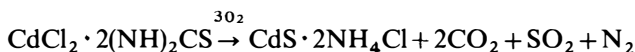
In the 15 years since the first publications (2, 25, 26), a great deal of work has been done on CdS. There is considerable disagreement among investigators about the mechanism of compound formation. The balanced chemical reaction that occurs during the deposition is



but Semenov et al (27) propose two possible mechanisms: (a) A hydrolysis involving the reaction products of thiourea with cadmium ions:



(b) A mechanism involving the $\text{CdCl}_2 \cdot (\text{NH}_2)_2\text{CS}$ complex, which decomposes above 210°C (2):



Infrared spectroscopy of films formed upon evaporation at 170°C showed the presence of the complex $\text{CdCl}_2 \cdot (\text{NH}_2)_2\text{CS} \cdot \text{H}_2\text{O}$, in which the H_2O is replaced by a second molecule of thiourea as the concentration ratio is

increased. If ammonia is added, the CdS begins to form at 170°C, indicating that the urea hydrolysis mechanism is involved.

Dutault & Lahaye (28) used x-ray diffraction and IR spectroscopy to study the complex and found that a second thiourea complex is formed upon heating. This complex decomposes to form CdS without passing through a liquid phase. Lamoreaux used a free-energy minimization computer program to study the thermodynamics of the CdS spray pyrolysis process (8). A nitrogen atmosphere was used, and the sulfur source was H₂S (assuming that the thiourea complex decomposes through an H₂S mechanism). The conclusions were that at low concentration (0.005 M) a slight excess of H₂S results in quantitative deposition of CdS, while at 0.01 M some CdCl₂ and a trace of CdSO₄ remain, even in a nitrogen atmosphere. At high concentration, representing H₂O evaporation, a tenfold excess of H₂S is needed to eliminate the chloride. The addition of 10% hydrogen to the nitrogen eliminates the sulfate but does not affect the CdCl₂. At higher temperatures (325 compared to 225°C), the chloride residual was a factor of 22 lower under equimolar conditions. The use of thermodynamics that assumes equilibrium conditions has its limitations; however, it is clear that the effects of temperature, concentration, and Cd/S ratio are significant and that the presence of excess thiourea is important in reducing the chloride content (29, 30).

As the thermodynamic study shows, the Cd/S ratio is an important variable (30–36). Although conditions vary and film thickness is an important factor (36), in general an excess of thiourea of up to 3 times the cadmium content of the spray solution leads to better crystallinity. The Cd/S ratio also has a strong influence on the efficiency of indium doping. The resistivity of 2-μm films is reduced significantly as the ratio is changed from a thiourea excess to a cadmium excess (to be published). Very little has been published on the doping of CdS films; resistivities of less than 1 Ω · cm have been achieved (37), and the effects of dopants on crystallinity and orientation have been reported (31).

The difficulties in knowing the actual substrate temperature have been discussed; however, the importance of the temperature of deposition is obvious from thermodynamic (8) and experimental evidence. Ma & Bube (13) investigated the effects of deposition temperature on the electrical, optical, and crystalline properties of spray-pyrolyzed CdS from 320 to 570°C heater temperature. Conductivity and mobility vary periodically with temperature of deposition (29–31, 34, 38, 39). Room temperature electron mobilities of up to 90 cm²/Vs (2) with resistivities of 10–100 Ω · cm have been reported. The layer thickness has a strong effect on the electrical properties (34, 40). Figure 2 shows that columnar grain increase in cross section, with layer thickness resulting in fewer grain boundaries and better

conductivity. Figure 3 shows the relationship between resistivity and thickness; this is very similar to vacuum-evaporated layers (41) particularly at $\sim 2\text{--}3\ \mu\text{m}$.

In an early publication, Micheletti & Mark (42) considered the barrier effects of grain boundaries on mobility (13, 39). The variation of mobility with temperature can be described by the expression $\mu = \mu_0 \exp(-\theta/kT)$, where θ can be interpreted as the barrier height to electron transport between grains of the film (13). The controlling factor again can be thickness. Micheletti & Mark used films that were $0.3\text{--}0.5\text{-}\mu\text{m}$ thick in their studies of the effect of oxygen absorption on the electrical properties, while others used $2\text{-}\mu\text{m}$ films (13, 39, 40).

The electronic properties of the grain boundaries are as critical as the grain size. Kwok (43) considered the two circumstances of insulating and "leaky" grain boundaries and found that a model based upon insulating grain boundaries was in better agreement with experimental observations. The fact that the carrier density is constant with thickness while the mobility increases, combined with the grain growth with thickness (Figure

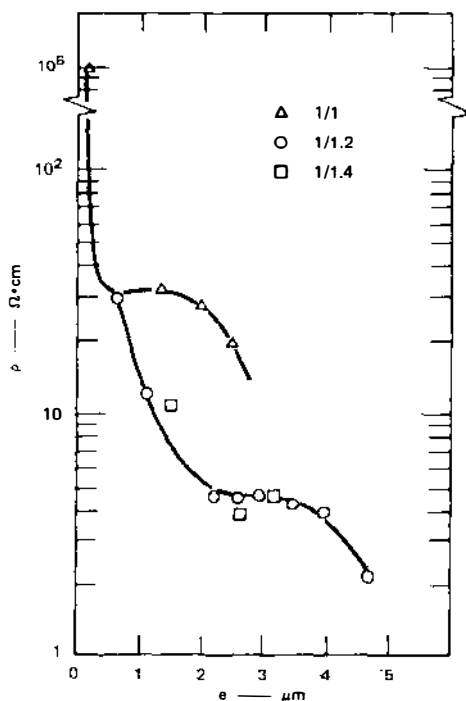


Figure 3 Resistivity of-sprayed films (after 34).

2), explains the change in resistivity with thickness. The absorption of oxygen on the crystallite surfaces can have a significant effect on the electronic properties of polycrystalline CdS films, including those prepared by spray pyrolysis (13, 29, 39, 42). The temperature dependence of the mobility as well as its magnitude are strongly influenced by the absorption of oxygen.

The structure of spray-pyrolyzed films is strongly dependent upon deposition conditions. CdS can exist in the hexagonal (wurtzite) or the cubic (zincblende or rock salt) structures (13, 44). The hexagonal films frequently exhibit preferred orientation; the extent and direction are influenced by the substrate temperature, the presence of dopants, and the Cd/S concentration ratio of the spray solution (2, 13, 18, 22, 25, 29, 30, 35, 44-46). Photoluminescence (47, 48) and thermoelectric effects (39, 40, 49) have been used to study the influence of grain boundaries on electronic properties of spray-pyrolyzed CdS.

When the cadmium source is the acetate (2, 16, 44, 50), amorphous films are obtained. It is even possible to produce the CdS films used for office copying that have a resistivity exceeding $10^{10} \Omega \cdot \text{cm}$ (Mooney-Brodie, patent applied for). These films grow in the columnar morphology (Figure 2) and exhibit many fascinating electronic and optical properties that depend closely on the substrate temperature. CdS films grown at temperatures above $\sim 300^\circ\text{C}$ are yellow, have sharp x-ray spectra (indicating they are in the wurtzite structure with the c axis parallel to the column axis), have relatively low resistivities that vary monotonically with Cl doping concentrations, and have a photoconductivity band gap near the normal crystalline value of 2.4 eV. Films grown below 200°C are brown. Their x-ray spectra are only slightly broader than those of the yellow films, and the principal lines are the same. The brown films have very high resistivities ($> 10^{12} \Omega \cdot \text{cm}$) that are unaffected by chlorine doping levels over many decades (up to 10^{19} cm^{-3}); the Fermi energy is evidently pinned near midgap. Photoconductivity sets in at photon energies of ~ 1.7 eV, well below the normal crystalline band gap, a result consistent with the brown color. The brown films convert to yellow if they are annealed above 300°C .

These phenomena can be explained by the following model: Each grain of the yellow film is an oriented single crystal. The grains of the brown films are also oriented, but there is a high density of stacking faults perpendicular to the c axis between the wurtzite and zincblende structures. This is plausible, because the metastable zincblende-structured CdS has been made and studied at room temperature. Thus the brown CdS is a disordered material in one direction and has many of the properties of amorphous semiconductors (51). In particular, the Fermi energy is pinned,

and there are disorder-scattering-induced band tails of the conduction or valence band states. There is a major difference between the behavior of this material, with its one-dimensional disorder, and that of true amorphous semiconductors. Amorphous semiconductors have optical conductivity band gaps that are larger than that of their crystalline state. However, the disordered CdS material has an effective band gap that is smaller than that of its crystalline form. There may or may not be mobility edges in the brown CdS, but there is some evidence from photoconductivity measurements in high fields to suggest their existence.

The alloys $\text{Zn}_{1-x}\text{Cd}_x\text{S}$ and $\text{Pb}_{1-x}\text{Cd}_x\text{S}$ have also been spray-deposited in the disordered form. As expected, the addition of Zn increases the effective band gap, while adding Pb decreases it. Thus, at least qualitatively, the spray-deposited disordered pseudo-binary¹ alloys behave like their single-crystal counterparts.

The crystallinity of the deposit is influenced by dopants (31, 40). The addition of large amounts of aluminum has been used to control the structure of spray-deposited films for photovoltaic applications (22, 30). The presence of Al_2O_3 as a second phase appears to inhibit the penetration of copper down grain boundaries during formation of the Cu_xS layer (22). Uekita et al (submitted for publication) showed that non-heat-treated films of less than $1\text{-}\Omega\cdot\text{cm}$ resistivity are obtained with indium doping. The Cd/S ratio in the spray solution strongly influences the doping efficiency.

The presence of residual chlorine is strongly influenced by deposition temperature and postdeposition heat treatment (8, 29, 30). It can be present as a second phase of CdCl_2 that is removed by heat treatment, and may actually act as a recrystallization flux in the process. The residual chlorine is a donor that can influence the resistivity, and in, turn, is sensitive to Cd/S ratios (36). Postdeposition heat treatment has been studied by many (2, 13, 29, 34–36, 39, 40, 42, 45). Crystallinity, resistivity, and mobility are influenced through the evolution of residual chlorine, fluxing by CdCl_2 residual, generation of sulfur vacancies, and the absorption-desorption of oxygen.

It is difficult to generalize about the properties of spray-pyrolyzed CdS and the effect of preparation variables. The dominant characteristic is the small grain size and the influence of grain boundaries on the properties of the film. The crystallite size is dependent on temperature, spray rate, and concentration, but the largest grains are produced by slow growth, which is not compatible with low-cost processing.

¹ A pseudo-binary alloy, e.g. $\text{Zn}_{1-x}\text{Cd}_x\text{S}$, is one in which there are S atoms on each sulfur-sublattice site on the zincblende lattice, but the zinc sublattice sites are occupied at random by Zn and Cd atoms with a probability weighted by the concentration x .

Other Compounds

A number of other II-VI compounds have been deposited by spray pyrolysis. CdSe is deposited from an aqueous solution of CdCl_2 and *N,N*-dimethylselenourea (52, 53). Selenourea is not stable; the dimethyl derivative decomposes in the light and must be protected, but it is stable in acidic solution (8). CdSe was first deposited in 1967 (2), but CdTe was not reported until 1981 (37, 48). Tellurourea or its derivatives are not stable, but aqueous solutions of CdCl_2 and TeO_2 will produce a CdTe deposit (37). (A reducing agent is required but details are not given.) ZnS and ZnSe were reported by Chamberlin & Skarman (2) without details. Ugai et al (50) studied ZnS sprayed from the acetate and chloride, producing semi-conducting films at 450°C substrate temperature.

PbS has been deposited from $(\text{NH}_2)_2\text{CS}$ and $\text{Pb}(\text{CH}_3\text{COO})_2$, PbCl_2 , and $\text{Pb}(\text{NO}_3)_2$. The IR spectra show that PbS is present in deposits sprayed from acetates at 100°C, but 200°C is necessary with chlorides. Residual PbO and $\text{Pb}(\text{CNS})_2$ were found in the acetate deposits, but films prepared from chloride solutions were free of IR-detectable impurities. The $\text{Pb}(\text{NO}_3)_2$ - $(\text{NH}_2)_2\text{CS}$ complex decomposes at 180°C, but $\text{Pb}(\text{NO}_3)_2$ residual persists up to 400°C (54). The resistivity and its temperature dependence are lower for those layers sprayed at 400°C than for those sprayed at 150°C (55).

The oxides of a number of group II metals have been prepared by decomposition of their acetates (56). ZnO has been studied most: Niikura et al (57) used ZnO spray-pyrolyzed from $\text{Zn}(\text{NO}_3)_2$ solution and a second film of vacuum-evaporated rhodamine B to study the sensitization mechanism of the dye. The dark resistivity of ZnO films is increased by a factor of 10^8 to as high as $10^{10} \Omega \cdot \text{cm}$ with baking in oxygen at 350°C. Although the light current I_L is also reduced, the I_L/I_D is greatly increased (58).

Aranovich et al (59, 60) studied ZnO films sprayed from ZnCl_2 and $\text{Zn}(\text{CH}_3\text{COO})_2$. The optical quality of acetate films was superior. Films deposited at substrate temperatures above 350°C show a sharp absorption edge at 3.3 eV. The dark resistivity is reduced from 10 to $10^{-2} \Omega \cdot \text{cm}$ with heat treatment in hydrogen at temperatures above 250°C. Thus, the resistivity of spray-pyrolyzed ZnO films can be varied over 12 orders of magnitude by heat treatment in hydrogen and oxygen. It is generally accepted that excess zinc atoms act as donors in ZnO (57), and reduction and oxidation explain the resistivity changes upon heat treatment. The presence of a surface depletion layer because of the chemisorption of oxygen further increases the resistivity (58). Preferred crystallographic orientation of ZnO films has been observed (61).

Pseudo-binary alloys have been deposited by spray pyrolysis. The structural and electronic properties of pseudo-binary III-V and II-VI semiconductor alloys always lie between those of the constituent materials. The lattice constant a of an alloy of $A_{1-x}B_x$ type, where A might represent ZnS and B represents CdS, has a concentration variation that closely approximates Vegards law:

$$a_{\text{alloy}} = a_{A_{(1-x)}} + a_{B_x}.$$

Electronic band structure quantities, in particular the band gap E_g and the reciprocals of the effective masses, have principal concentration variations that are like Vegards law. However, there are quadratic deviations from the linear concentration dependence. Thus the alloy band gap E_g^{alloy} is related to the constituent material gaps by expressions of the form

$$E_g^{\text{alloy}} = E_g^A(1-x) + E_g^Bx - bx^2,$$

where b is called a bowing parameter. Note that the alloy band gap is always smaller than one would judge from the linear approximation. The bowing parameter b is small for alloys made of constituents with similar potentials, e.g. $\text{Ga}_{1-x}\text{Al}_x\text{As}$, and large for most II-VI compound alloys, whose potentials are more ionic and often quite different.

Vacuum evaporation is a common method for preparing alloy films, but it is often necessary to resort to using two sources in the preparation of binary alloy films with careful control of source temperature in order to obtain a reproducible ratio of the constituents. In spray pyrolysis, the concentration of the constituents in the solutions fixes the composition in the film for any temperature and spray rate. The ratios in the solution and the film are not always the same, for example, $\text{CdS}_x\text{Se}_{(1-x)}$ films have been observed whose Se/S ratios were 8% richer than the sprayed solutions (40, 62). This alloy is very useful for the production of a panchromatic photoconductor (2, 63). The band gap of the alloy can be varied from 2.42 to 1.72 eV as x varies from 1 to 0. The resistivity of this alloy does not vary appreciably with the ratio (40, 62).

A great deal more has been done on the $\text{Zn}_x\text{Cd}_{1-x}\text{S}$ alloys because of their utility in solar cells (64, 65). The as-sprayed films have been as much as 20% richer in Cd than the solution (62). The band gap varies from 2.42 to 3.66 eV with some bowing (61, 66). CdS films are usually of the wurtzite hexagonal crystal structure, while ZnS is cubic (zincblende). The conversion from one structure to the other occurs at $x = 0.8$ (66). The resistivity of ZnS films is 10^{10} times that of CdS and varies almost linearly with x (38, 62, 67–72). In the as-sprayed films, the electron concentration varies sharply with x , but after heat treatment in nitrogen for 10 min at 300°C the effect of x is very small. The mobility also varies with x but is little influenced by heat

treatment (67). A resistivity of $6.9 \Omega \cdot \text{cm}$ after heat treatment was reported for a film with $x = 0.19$. Indium doping was effective in reducing the resistivity of an as-sprayed film with $x = 0.1$ from 10^4 to $\leq 10^2 \Omega \cdot \text{cm}$ (70).

In addition to compound semiconductor alloys, ternary and quaternary compounds have been deposited by Pamplin & Feigelson (73, 74). In the I-III-VI₂ series, they reported on 16 compounds of the general composition $\text{Cu}(\text{Ga}_x\text{In}_{1-x})(\text{S}_y\text{Se}_{1-y})_2$ (74) and four defect compounds of the type $\text{Cu}(\text{Ga}_x\text{In}_{1-x})_5\text{S}_2(\text{S}_y\text{Se}_{1-y})_8$ (73). They also produced four compounds of the family Cu_2Zn (or Cd) SnS (or Se)₂ and four of the composition Cu_2In (or Ga) SnS (or Se)₄ (73). In this broad study of spray deposition they reported the lattice constants, energy gap, conductivity type, and resistivity of the films (73, 74). Gorska et al (75) deposited AgInS_2 and AgIn_5S_2 and AgIn_5S_8 as well as CuInS_2 (76) for solar cell applications.

All of the preceding studies of the ternary and quaternary alloys resulted in films of the sphalerite crystal structure, although the chalcopyrite was expected. It is possible to produce chalcopyrite CuInSe_2 by using a 10% excess of copper and 100% excess selenium over the stoichiometric quantities and heating at or above 400°C for 10 min to effect the phase transformation (8). The deposition is not efficient above 350°C (6), and a postdeposition heat treatment in nitrogen, preferably at 600°C , is required for conversion. The requirement of an excess over the stoichiometric quantity in the spray solution is not unique. Feigelson et al (62) found a difference between the solution and film composition for the II-VI alloys discussed earlier. Thermodynamic and experimental studies showed that for CuInSe_2 , an excess of selenium is necessary to avoid the presence of Cu_{2-x}Se as a second phase. Elemental selenium is present as a second phase when an excess of *N,N*-dimethylselenourea is used, although it is not readily detectable by optical or x-ray methods (8). Excess selenium is required for stoichiometry, and the sphalerite form is present in the as-sprayed film, requiring a postdeposition heat treatment in nitrogen, or preferably H_2 - H_2Se , atmosphere to produce a stoichiometric film of the chalcopyrite structure that is free of the second-phase selenium and of oxygen impurities.

The oxides and sulfides of many metals have been deposited by spray pyrolysis, and starting materials, solvents, and conditions of spraying have varied greatly. Table 1 lists some of the materials sprayed. As early as 1951, a patent was issued (1) citing the spraying of SnCl_4 , both by itself and with dopants such as antimony, copper, iron, manganese, vanadium, zinc, and bismuth. Some of the claims also cite spraying indium or mixtures of metal salts to give tin-antimony and indium tin oxide (ITO) films. Dopants claimed were varied and as much as 20% in these films. This was actually the first spray pyrolysis process, although the CdS deposition (2) is usually cited.

Table 1 Sprayable materials

Film	Starting Materials	Solvents	References
SnO ₂	SnCl ₄	H ₂ O + HCl	1, 7, 78, 79
		H ₂ O + alcohol	9, 15, 80, 81, 82
	SnCl ₂	Ethanol	5, 56, 83, 84
	SnBr ₄	HBr	78
	(NH ₄) ₂ SnCl ₆	H ₂ O	85, 86
	(CH ₃ COO) ₂ SnCl ₂	Ethyl acetate	86
In ₂ O ₃	InCl ₃ or InCl ₂	Butyl acetate or butanol	19, 77
	Indium acetylacetonate	Acetylacetone	7
	InCl ₃	Methanol-water	9, 56
ITO	InCl ₃ , SnCl ₄	Methanol-water or ethanol-water	9, 15, 87, 88
Cu ₂ S	Cu(C ₂ H ₃ O ₂) ₂ + thiourea	Water	45
PbS	Pb(CH ₃ COO) ₂ , PbCl ₂ , or Pb(NO ₃) ₂ + thiourea	Water	56
PbO	PbCl ₂	Water	56
Cr-Co oxides	Cr acetylacetonate + Co acetylacetonate	Toluene-methanol	90
Cr ₂ O ₃	Cr acetylacetonate	Butanol	7
Fe ₂ O ₃	Iron acetylacetonate	Butanol	7
V ₂ O ₃	Vanadium acetylacetonate	Butanol	7
Pd	Palladium acetylacetonate	Butanol	7
Ru	Ruthenium acetylacetonate	Butanol	7
CdSnO ₄ , CdSnO ₃	CdCl ₂ + SnCl ₄	HCl	91, 92, 69
CuInSe ₂	InCl ₃ , CuCl, N, N-dimethylselenourea	H ₂ O	6, 74
CuInS ₂	InCl ₃ , CuCl or CuCl ₂ , N, N-dimethylthiourea	H ₂ O	6, 74
CuGaS ₂	CuCl or CuCl ₂ , GaCl ₂ , N, N-dimethylthiourea	H ₂ O	6, 73, 74
CuGaSe ₂	CuCl or CuCl ₂ , GaCl ₂ , N, N-dimethylselenourea	H ₂	6, 73, 74
ZnO	ZnCl ₂	Water	56
B ₂ O ₃	Boron chloride	Water	56
Al ₂ O ₃	Al Cl ₃	Water	56

Groth (19) used InCl₃ in butyl acetate or butanol and sprayed on borosilicate glass at temperatures of 350 to 500°C. He found that the temperature on the plate during spraying dropped about 5°C. If the In₂O₃ formed in the hot-air layer just above the plate, the film was cloudy; the transition had to take place on the plate to form a clear film. Doping gave films with conductivities between 1.5×10^2 and $4.3 \times 10^3 \Omega^{-1} \text{ cm}^{-1}$.

Raza et al (77) used InCl₃ in butyl acetate and sprayed on a heated glass substrate at 500°C. Because the spraying was done in air, annealing at

300°C under high vacuum was necessary to remove the defects. The absorption of the films was determined. Viguié & Spitz (7) sprayed indium acetylacetonate in acetylacetone. Spraying InCl_3 from a methanol-water mixture was another common procedure (9, 56).

However, most work with indium has been with the alloy ITO. Both InCl_3 and SnCl_4 are dissolved in an alcohol-water mixture; as it is sprayed, the reaction taking place forms ITO (9, 15, 80, 86, 87). Electrical and optical characteristics of the films are evaluated in relationship to temperature of fabrication. Pommier et al (9) found that for ITO, optimum parameters were $T = 450^\circ\text{C}$, $\text{Sn/In} = 0.025$, and flow rate = 3 ml/min. Manificier & Szepessy (89) used atomic ratios of Sn/In of 0.023 with borosilicate substrates and a ratio of 0.025 with silicon substrates. Substrate temperatures of 498 and 435°C respectively gave the best overall results. The general range of substrate temperature for ITO preparation used in all the investigations mentioned above was 400 to 500°C and Sn/In ratios all were around 0.025.

The most work in transparent films recently has been with tin oxide. The starting materials are varied, ranging from $(\text{NH}_4)_2\text{SnCl}_6$ or $(\text{CH}_3\text{COO})_2\text{SnCl}_2$ (86) to the commonly used SnCl_4 (5, 77–79, 81, 82, 84). A few studies have been made using dopants such as antimony (5, 81, 82). Pommier et al (9) tried fluorine as a dopant, but the results for SnO_2 were not as good as ITO. Rohatgi et al (81) tried PCl_5 , InCl_3 , and Ti as dopants and found that large additions ($> 6\%$) of Sb , P , Ti , and In increased the activation energy and resistance but reduced charge carrier concentrations. Kim & Laitinen (78) used SnBr_4 in HBr to make SnO_2 films and found wide variations in surface conductivity at different temperatures between the chloride and bromide preparations, with the bromides having the lower surface conductivity in each case. A good review on SnO_2 films is that by Sanz Maudes & Rodrigues (5).

Other oxide films such as ZnO , PbO , B_2O_3 , and CdO were prepared by spraying the metal chlorides onto silicon substrates at about 500°C (56). Annealing at temperatures above 900°C was necessary to form bonds between the metal and silicon.

Haacke et al (91, 92) worked with cadmium stannate films, and both Cd_2SnO_4 and CdSnO_3 were spray products. If required deposition conditions are maintained, only one or the other phase is obtained. Substrate temperatures above 800°C give Cd_2SnO_4 , while temperatures of less than 800°C lead to CdSnO_3 . If the substrate temperature is in the range of 400 to 500°C , translucent or opaque coatings result.

Noguchi & Mizuhashi (90) worked with cobalt and chromium oxide films to study the effect of substrate temperature on the deposition rate. Because of the nonequilibrium conditions in the rapidly proceeding

Table 2 Spray-pyrolyzed solar cells

Heterojunction	V_{oc}	I_{sc} (mA)	J_{sc} (mA/cm ²)	ff	η	Reference
CdS/Cu _x S _y ^a	0.44	3.7			3.5	3,4
CdS/Cu ₂ S					4.2 - 4.92	11
CdS/Cu ₂ S	0.42	22.9	22.9	0.62	6.0	12
CdS/Cu ₂ S ^a	0.28		2.2			93
CsS/Cu ₂ S (undoped)	0.35		11	0.5	2.0	30
CdS/Cu ₂ S (Al doped)	0.39		19	0.41	3.5	
CdS/Cu ₂ S	0.35 - 0.42		1.7 - 1.2		1.0	94
CdS/Cu ₂ S	0.32		7.5		1.2	
Cd _{0.95} Zn _{0.05} /Cu ₂ S	0.38		5.0		0.98	68
Cd _{0.9} Zn _{0.1} /Cu ₂ S	0.37		3.1		0.47	
Cd _{0.9} Zn _{0.1} /Cu ₂ S	0.44		4.8		1.1	
Cd _(1-x) Zn _x S/Cu ₂ S x=0	0.58		18.7			66
x=0.55	0.78		1.9			
CdS/Cu ₂ S	0.53, 0.40	19, 15		0.66, 0.67	6.7, 4.0	
Cd _{0.9} Zn _{0.1} /Cu ₂ S	0.58, 0.43	12, 19		0.67, 0.65	4.8, 5.6	
Cd _{0.8} Zn _{0.2} /Cu ₂ S	0.63, 0.50	10, 15		0.65, 0.55	4.0, 3.55	95
Cd _{0.7} Zn _{0.3} /Cu ₂ S	0.64, 0.53	5, 5		0.69, 0.48	2.4, 1.3	
Cd _{0.6} Zn _{0.4} /Cu ₂ S	0.58	1		0.45	1	
Cd _(1-x) Zn _x /Cu ₂ S x=0	0.40	17		0.7	4.0	
x=0.1	—	—		—	5.6	96
x=0.4	0.59	1		0.45	—	

CdS/CdTe	0.53 - 0.72	16.4 - 10.5	0.63 - 0.62	6.5 - 5.5	97, 98, 99
Cd _{0.9} Zn _{0.1} /CdTe	0.79 - 0.82	12.7 - 10.8	0.64 - 0.56	7.8 - 6.0	
CdS/CdTe (No H.T.)	0.55	1.8	0.37	0.4	
H ₂ - 360°C - 15 min	0.62	5.8	0.49	2.1	100
H ₂ - 420°C - 5 min	0.66	9.8	0.58	4.1	
CdS/CdTe	0.53 - 0.74	3.9 - 13.2	0.62	2.1 - 6.1	13
CdS/CdTe ^a	0.635	12.9	0.49	4.0	37
ZnO/CdTe	0.54	18.2 - 21.1	0.50	8.8 - 9.2	101
CdS/CuInS ₂ ^a	0.1 - 0.25	0.8 - 0.004	-	-	76
CdS/CuInSe ₂ ^a	0.25	7.2	0.2	<0.5	8
ITO/n-Si	0.5 - 0.53	31 - 41	0.7 - 0.45	10 - 11.5	87, 88, 89
ITO/n-Si (poly)	0.5	36	0.46	9.1	87
CdS/NaOH - Na ₂ S	0.6	1.8 x 10 ⁻³	0.4	0.04	102
ITO/CdSe/NaOH - Na ₂ S - S	0.63	11.8	0.35	5.2 - 7.8	52

^aAll layers deposited by spray pyrolysis.

reaction near the surface, the true temperature was difficult to measure. However, differences in the Co/Cr ratio in the films were found to be critically dependent on the substrate temperatures. Marucchi et al (45), working with CdS and Cu_xS , also found variations in the deposition rate with substrate temperature.

DEVICE APPLICATIONS

The major interest in spray pyrolysis is for low-cost manufacturing processes. The only important commercial process at present is for the deposition of a transparent conductive layer on glass (1). Solar cells prepared by spray pyrolysis have been studied by many investigators, as summarized in Table 2, starting with that of Chamberlin and co-workers (3, 4). Jordan (11, 23) suggested an all spray process, starting with hot float glass as it exits from the glass plant, using the residual process heat by spraying on the glass before it is removed from the molten tin; although the IR lamps are now used (12), the suggested back-wall cell was of the configuration $\text{glass}/\text{SnO}_x/\text{n-CdS}/\text{p-Cu}_2\text{S}/\text{Cu}$. An evaporated Inconel-aluminum contact was proposed for the SnO_x/CdS n-type region and evaporated copper for the Cu_xS . The cost advantage of the spray process over vacuum evaporation for semiconductor deposition is obvious. The cell configuration with the glass surface exposed to sun and weather also reduces cost, in that the glass is both the encapsulant and the substrate. The backside encapsulant can be a polymer, which need not be exposed to sunlight and subject to photodegradation. Except for the first reports (2, 4, 45), spray pyrolysis of the Cu_xS has not been successful, and cells now use the chemical ion-exchange method of dipping the CdS film into an aqueous solution of CuCl or evaporation of the CuCl and heat treatment. This process is now in the pilot plant stage and produces 1-cm^2 cells of 6% efficiency, but panels are limited to 3% (12). Other cells in which the p-type layer is deposited by spray pyrolysis have recently been produced (8, 37, 76). Spray pyrolysis of n-type layers on single crystals have been successful, particularly for SnO_x and ITO on silicon (see Table 2). Chevalier & Deunas (103) sprayed SnO_x on both sides of a silicon p-n junction to form a bifacial cell.

Spray pyrolysis has been applied to silver mirror formation by the classical ammoniacal reducing solution (104), the preparation of CdSe heterojunction vidicon targets (53), and cathodoluminescent phosphor films (105). Manificier & Fillard (15) suggested that the high IR reflectivity of sprayed ITO films makes them good candidates for coating the glazing of solar thermal absorbers that use the greenhouse effect.

SUMMARY

Spray pyrolysis is a convenient, low-cost, and rapid method for the deposition of thin films, and has been used for about 30 years for the manufacture of conductive glass (1). It is also an excellent method for preparing films of semiconductor alloys and complex compounds. In the case of the copper ternaries and quaternaries, it was a simple method for studying a broad range of alloys that had not been prepared before (6, 74) by varying the quantities of stock solutions.

Because individual droplets evaporate and react very quickly, grain sizes are very small, usually less than $0.1\ \mu\text{m}$. The small grains are a disadvantage for most semiconductor applications. The use of low concentration and slow spray rates to improve film quality tends to frustrate the low-cost processing objective, but postdeposition heat treatment of small-grain films can improve stoichiometry and crystallinity.

The process is sensitive to variables, particularly temperature, and the measurement at the surface is uncertain. Not only do the physical and electronic properties of the film vary with temperature, but the deposition efficiency decreases with increased temperature; stoichiometry is also affected, particularly for alloys. In spite of these difficulties, spray pyrolysis is an excellent method for the deposition of large-area thin films.

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Literature Cited

1. Mochel, J. M. 1951. *US Patents* 2,564,707; 2,564,987; 2,564,709; 2,564,710; 2,564,708; 2,564,706
2. Chamberlin, R. R., Skarman, J. S. 1966. *J. Electrochem. Soc.* 113(1): 86-89
3. Chamberlin, R. R., Skarman, J. S., Koopman, D. E., Blakely, L. E. Jr. 1963. *Tech. Doc. Rep. ASD-TDR-63-223, Part I*, AD403 053. Washington, DC: NTIS
4. Chamberlin, R. R., Skarman, J. S. 1966. *Solid State Electron.* 9: 819-23
5. Sanz Maudes, J., Rodrigues, T. 1980. *Thin Solid Films* 69(2): 183-90
6. Pamplin, B. R. 1979. *Prog. Cryst. Growth Charact.* 1(4): 395-403
7. Vigić, J. C., Spitz, J. 1975. *J. Electrochem. Soc.* 122(4): 585-88
8. Mooney, J. B., Lamoreaux, R. H., Bates, C. W. Jr. 1981. *SERI Subcontract XS-9-8104-4*, Menlo Park, Calif: SRI Int.
9. Pommier, R., Gril, C., Marucchi, J. 1981. *Thin Solid Films* 77: 91-97
10. Singh, V. P. 1978. *IEEE Photovoltaic Specialists Conf., 13th, Washington DC, 1978*. Piscataway, NJ: IEEE
11. Jordan, J. F. 1975. *IEEE Photovoltaic Specialists Conf., 11th, Scottsdale, Ariz., 1975*. Piscataway, NJ: IEEE
12. Roderick, G. A. 1980. *Proc. Eur. Community Photovoltaic Solar Energy*

- Conf., 3rd, Cannes*, pp. 327-34. Dordrecht, Holland: Reidel
13. Ma, Y. Y., Bube, R. H. 1977. *J. Electrochem. Soc.* 124(9): 1430-35
 14. Lampkin, C. M. 1979. *Proc. European Community Photovoltaic Solar Energy Conf., 2nd, Berlin*, pp. 396-405. Dordrecht, Netherlands: Reidel
 15. Manificier, J. C., Fillard, J. P. 1981. *Thin Solid Films* 77: 67-80
 16. Alae, M. S., Rouhani, M. D. 1977. *Proc. Int. Conf. Photovoltaic Solar Energy, Luxembourg*, pp. 1151-59. Dordrecht, Netherlands: Reidel
 17. Minoura, H., Nakamura, T., Ueno, Y., Tsuiki, M. 1977. *Chem. Lett.* 1977(8): 913-16
 18. Tsuiki, M., Minoura, H., Nakamura, T., Ueno, Y. 1978. *J. Appl. Electrochem.* 8(6): 523-29
 19. Groth, R. 1966. *Phys. Status Solidi* 14: 69-75
 20. Lampkin, C. M. 1979. *Prog. Cryst. Growth Charact.* 1(4): 406-16
 21. See Ref. 14
 22. Berg, R. S., Nasby, R. D., Lampkin, C. 1978. *J. Vac. Sci. Technol.* 15(2): 359-62
 23. Jordan, J. F. 1976. *Proc. ERDA Semiannual Solar Photovoltaic Conversion Program Review, 2nd, Lake Buena Vista, Fla.*, pp. 299-320. Washington, DC: NTIS
 24. Blandenet, G., Lagarde, Y., Spitz, J. 1975. *Proc. Conf. Vapor Deposition*, pp. 190-203. Princeton, NJ: Electrochem. Soc.
 25. Chamberlin, R. R. 1966. *Am. Ceram. Soc. Bull.* 45(8): 698-701
 26. Hill, J. E., Chamberlin, R. R. 1964. *US Patent* 3,148,084
 27. Semenov, V. N., Averbakh, E. M., Mikhaleva, L. A. 1979. *Zh. Neorg. Khim.* 24(4): 911-15
 28. Dutault, F., Lahaye, J. 1979. *Bull. Soc. Chim. Fr.* 1(5-6): 145-49
 29. Dutault, F., Lahaye, J. 1980. *Rev. Phys. Appl.* 15(3): 579-84
 30. Perotin, M., Bougnot, J., Oudeacoumar, Marucchi, J., Marjan, M., Savelli, M. 1980. *Rev. Phys. Appl.* 15(3): 585-93
 31. Gupta, B. K., Agnihotri, O. P. 1978. *Philos. Mag.* 37B: 631-33
 32. Gupta, B. K., Agnihotri, O. P. 1977. *Solid State Commun.* 23(5): 295-300
 33. Gupta, B. K., Agnihotri, O. P., Raza, A. 1978. *Thin Solid Films* 48(2): 153-62
 34. Bougnot, J., Perotin, M., Marucchi, J., Sirkis, M. 1976. *IEEE Photovoltaic Specialists Conf., 12th, Baton Rouge, La.*, pp. 519-25. Piscataway, NJ: IEEE
 35. Martinuzzi, S., Oualid, J., Cabanebrouty, F., Mostavan, A., Gervais, J. 1979. *Rev. Phys. Appl.* 14(1): 237-43
 36. Recktenwald, J., Mooney, J. B., McIntosh, L., Lamoreaux, R. H., Bates, C. W. Jr., Raza, A., Nelson, K. 1981. *Proc. Electrochem. Soc.* 81(1): 692-94
 37. Serreze, H. B., Lis, S., Squillante, M. R., Turcotte, R., Talbot, M., Entine, G. 1981. *IEEE Photovoltaic Specialists Conf., 15th, Kissimmee, Fla.*, pp. 1068-72. Piscataway, NJ: IEEE
 38. Kwok, H. L., Chan, Y. C. 1980. *Thin Solid Films* 66: 303-9
 39. Wu, C. H., Bube, R. H. 1974. *J. Appl. Phys.* 45(2): 648-60
 40. Feigelson, R. S. 1974. *Photoelectric Properties of Chemically Deposited Cadmium-Sulfoselenide Films*. PhD thesis. Stanford Univ., Stanford, Calif. 105 pp.
 41. Wilson, J. I. B., Woods, J. 1973. *J. Phys. Chem. Solids* 34: 171-81
 42. Micheletti, F. B., Mark, P. 1967. *Appl. Phys. Lett.* 10(4): 1368
 43. Kwok, H. L. 1980. *J. Phys. D* 13: 1911-23
 44. Alae, M. S., Rouhani, M. D. 1979. *J. Electron. Mater.* 8(3): 289-302
 45. Marucchi, J., Perotin, M., Oudeacoumar, Savelli, M. 1978. See Ref. 10, pp. 298-302
 46. Chen, W.-C., Walker, T. P., Feldman, B. J. 1980. *Solid State Commun.* 36: 915-16
 47. Feldman, B. J., Boone, J. L., Van Doren, T. 1981. *Appl. Phys. Lett.* 38: 703-5
 48. Feldman, B. J., Duisman, J. A. 1980. *Appl. Phys. Lett.* 37(12): 1092-93
 49. Wu, C.-H. 1973. *Photothermoelectric Analysis of Electrical Transport in Films of Cadmium Sulfide*. PhD thesis. Stanford Univ., Stanford, Calif.
 50. Ugai, Y. A., Semenov, V. N., Averbakh, E. M. 1978. *Inorg. Mater. USSR* 14(8): 1196-97
 51. Mott, N. F., Davis, E. A. 1979. *Electronic Processes in Non-Crystalline Materials*. Oxford: Clarendon. 583 pp. 2nd ed.
 52. Liu, C.-H. J., Wang, J. H. 1980. *Appl. Phys. Lett.* 36(10): 852-53
 53. Jedlicka, M., Ladman, R., Vitovsky, O., Lexas, D., Srb, I. 1976. *Adv. Electron. Electron Phys.* 40: 323-33
 54. Semenov, V. N., Averbakh, E. M., Ugai, Y. A. 1980. *Zh. Prikl. Khim. (Moscow)* 53(1): 30-34
 55. Tyagi, R. C., Agarwal, S. K., Sethi, V. C. 1977. *Indian J. Pure Appl. Phys.* 15(9): 670-72
 56. Semenov, V. N., Baenko, Y. E., Averbakh, E. M., Anokhin, V. Z., Mittova, I. Y. 1978. *Inorg. Mater. USSR* 14(2): 193-95
 57. Niikura, I., Watanabe, H., Wada, M. 1973. *Jpn. J. Appl. Phys.* 12(5): 657-60
 58. Nobbs, J. McK., Gillespie, F. C. 1970. *J. Phys. Chem. Solids* 31(10): 2353-59

59. Arnovich, J., Ortiz, A., Bube, R. H. 1979. *J. Vac. Sci. Technol.* 16(4): 994-1003
60. Fahrenbruch, A. L., Aranovich, J., Courreges, F., Chynoweth, T., Bube, R. H. 1978. See Ref. 10, pp. 281-87
61. Janda, M., Kubovy, A. 1976. *Krist. Tech.* 11(10): K53-56
62. Feigelson, R. S., N'Diaye, A., Shaiw-Yih, Y., Bube, R. H. 1977. *J. Appl. Phys.* 48(7): 3162-64
63. Skarman, J. S. 1965. *Solid State Electron.* 8: 17-29
64. Burton, L. C. 1980. *Solar Cells* 1(2): 159-74
65. Burton, L. C., Baron, B., Devaney, W., Hench, T. L. 1976. See Ref. 34, pp. 526-27
66. Singh, V. P., Jordan, J. F. 1981. *IEEE Electron Device Lett.* 2: 137-38
67. Chynoweth, T. A., Bube, R. H. 1980. *J. Appl. Phys.* 51(3): 1844-46
68. Chow, L. W., Kwok, H. L. 1981. *J. Phys. D* 14: 463-69
69. Agnihotri, O. P., Gupta, B. K. 1978. See Ref. 10, pp. 195-99
70. Agnihotri, O. P., Gupta, B. K. 1979. *Jpn. J. Appl. Phys.* 18(2): 317-20
71. Agnihotri, O. P., Gupta, B. K., Thangaraj, R. 1979. *Solid State Electron.* 22(2): 218-20
72. Banerjee, A., Nath, P., Vankar, V. D., Chopra, K. L. 1978. *Phys. Status Solidi* 46A(2): 723-28
73. Pamplin, B. R., Feigelson, R. S. 1979. *Mater. Res. Bull.* 14(1): 1-4
74. Pamplin, B. R., Feigelson, R. S. 1979. *Thin Solid Films* 60(2): 141-46
75. Gorska, M., Beaulieu, R., Loferski, J. J., Roessler, B. 1980. *Thin Solid Films* 67(2): 341-45
76. Gorska, M., Beaulieu, R., Loferski, J. J., Roessler, B. 1979. *Sol. Energy Mater.* 1(3-4): 313-17
77. Raza, A., Agnihotri, O. P., Gupta, B. K. 1977. *J. Phys. D* 10: 1871-76
78. Kim, H., Laitinen, H. A. 1975. *J. Am. Ceram. Soc.* 58(1-2): 23-25
79. Nagatomo, T., Endo, M., Omoto, O. 1979. *Jpn. J. Appl. Phys.* 18(6): 1103-9
80. Manificier, J. C., deMurica, M., Fillard, J. P. 1975. *Mater. Res. Bull.* 10(2): 5-20
81. Rohatgi, A., Viverito, T. R., Slack, L. H. 1974. *J. Am. Ceram. Soc.* 57(6): 278-79
82. Peaker, A. R., Horsley, B. 1971. *Rev. Sci. Instrum.* 42(12): 1825-27
83. Aitchison, R. E. 1954. *Aust. J. Appl. Sci.* 5: 10-17
84. Miloslavskii, V. K. 1959. *Opt. Spectrosc. USSR* 7(2): 154-56
85. Chambouleyron, I., Saucedo, E., Montoy, J. 1979. See Ref. 14, pp. 647-53
86. Pink, H., Treitinger, L., Vite, L. 1980. *Jpn. J. Appl. Phys.* 19(3): 513-17
87. Schunck, J. P., Coche, A. 1979. *Appl. Phys. Lett.* 35: 863-65
88. Ashok, S., Sharma, P. P., Fonash, S. J. 1980. *IEEE Trans. Electron Devices* 27: 725-29
89. Manificier, J. C., Szepessy, L. 1977. *Appl. Phys. Lett.* 31(7): 459-62
90. Noguchi, S., Mizuhashi, M. 1981. *Thin Solid Films* 77: 99-106
91. Haacke, G., Burton, L. C. 1976. *NSF/RANN/SE/AER73-07957/PR75/4, NSF/RA-760012, PB-253 007/9GA.* 54 pp. Washington, DC: NTIS
92. Haacke, G., Ando, H., Mealmaker, W. F. 1977. *J. Electrochem. Soc.* 124(12): 193-96
93. Vedel, J., Cowache, P., Dachraoui, M. 1980. *Rev. Phys. Appl.* 15: 1521-28
94. Siu, W. C., Kwok, H. L. 1978. *J. Phys. D* 11(5): 669
95. Das, S. R., Banerjee, A., Chopra, K. L. 1979. *Solid State Electron.* 22(6): 533-39
96. Banerjee, A., Das, S. R., Thakoor, A. P., Randhawa, H. S., Chopra, K. L. 1979. *Solid State Electron.* 22(5): 495-99
97. Bube, R. H. 1977. *Proc. Soc. Photo-Opt. Instrum. Eng.* 114: 7-13
98. Yin, S.-Y., Fahrenbruch, A. L., Bube, R. H. 1978. *J. Appl. Phys.* 49(3) (Pt. 1): 1294-96
99. Bube, R. H., Buch, R., Fahrenbruch, A. L., Ma, Y. Y., Mitchell, K. W. 1977. *IEEE Trans. Electron Devices* 24(4): 487-92
100. Ma, Y. Y., Fahrenbruch, A. L., Bube, R. H. 1977. *Appl. Phys. Lett.* 30(8): 423-24
101. Aranovich, J., Golmayo, D., Fahrenbruch, A. L., Bube, R. H. 1980. *J. Appl. Phys.* 51(8): 4260-68
102. Tsou, C. C., Cleveland, J. R. 1980. *J. Appl. Phys.* 51(1): 455-58
103. Chevalier, Y., Deunas, F. 1979. See Ref. 14, pp. 817-23
104. Armstrong, B. 1977. *Appl. Opt.* 16(11): 2785-87
105. Gilliland, J. W., Hall, M. S. 1967. *Electrochem. Technol.* 5: 303-6



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