Appl. Phys. A 57, 19–24 (1993)

Applied Physics A Solids and Surfaces

Transparent Conductive Electrodes for Electrochromic Devices: A Review

C. G. Granqvist

Department of Physics, Chalmers University of Technology and University of Gothenburg, S-41296 Gothenburg, Sweden (Fax: +46-31/7723357)

Received 19 October 1992/Accepted 10 March 1993

Abstract. This paper reviews the optical and electrical performance of thin films that are useful as transparent electrodes in electrochromic devices. The properties of certain heavily doped wide-bandgap semiconductor oxides (especially $In_2O_3:Sn$) and of certain coinage metal films are discussed.

PACS: 78.65, 42.70, 81.15, 85.60

Almost all practically useful electrochromic devices must incorporate optically transparent electrodes. They are required for transporting electrons to and from the electrochromic layer as well as for providing a distributed electric field within which ions are moved. A reflecting device needs one such electrode on the side that is to be viewed, whereas a transmissive device requires two transparent electrodes. The electrode can be applied directly onto the surface of a transparent substrate, or it can form the top layer in a multilayer stack in an all-solid-state inorganic device. For devices with liquid or polymeric electrolytes, the coated substrate can provide encasement and protection. In most devices it is an advantage if ion permeation into the transparent electrode is small, whereas for other devices such permeation is essential for their functioning.

Two groups of materials are of prime interest as transparent electrodes: The first group contains a number of heavily doped wide-bandgap oxide semiconductors with typical film thicknesses of a few times 0.1 μm. Their fabrication requires precise stoichiometric control, and the deposition rate is low. Properly made they are hard, compact, strongly adherent to glass, and chemically inert. The electrical resistivity ϱ is rather independent of film thickness. The luminous and near-infrared absorptance can be very small, but the films are prone to show some iridescence due to thickness variations over extended surface areas.

The second group of transparent electrodes embrace coinage metals with typical film thicknesses of a few times 0.01 μm. Such films can be made without stoichiometric control and at high deposition rates; they are soft, porous, sometimes poorly adherent to substrates, catalytically active, and chemically reactive depending on the actual conditions. The electrical resistivity is strongly thickness dependent, and the optical properties are characterized by absorption but not iridescence.

We note that, whereas ϱ is the fundamental property, electrochromic device performance is often governed by the "resistance per square" defined by

$$R_{\mathrm{sq}} = \varrho t\,, \tag{1}$$

which typically should lie in the range 1 Ω to 100 Ω. Here t denotes film thickness.

Below we discuss the science and technology of transparent conductive electrodes. The presentation is rather brief, but it gives ample references to prior work. It is hoped that this paper could provide an easy access to the pertinent scientific and technical literature. The properties of transparent electrodes are reviewed from a general viewpoint in [1–13] and from the viewpoint of electrochromics in [14, 15].

1 Thin Films of Doped Oxide Semiconductors

Transparent electrodes based on doped oxide semiconductors make use of a wide-bandgap host material – normally of In_2O_3, SnO_2 or ZnO – which is doped either by substitution of some of the atoms or by oxygen vacancies. At the moment, the most viable alternatives are $In_2O_3:Sn$ (also called Indium Tin Oxide or ITO), $SnO_2:F$, $SnO_2:Sb$ and ZnO:Al.

A consistent and fairly detailed theoretical model has emerged from recent work [8, 16–20]. The optical and electrical properties can be described by use of an effective mass model for n-doped semiconductors well above the Mott critical density. At the high doping levels that are of practical interest, the impurities are singly ionized and the associated electrons occupy the bottom of the conduction band in the form of an electron gas. A straight-forward generalization to doping by doubly ionized oxygen vacancies in SnO_x has been made recently [21]. The ionized impurities behave approximately as point scatterers, which, at least for $In_2O_3:Sn$, is consistent with pseudopotential arguments. Screening of the ions can be described through the random phase approximation [22], which works well as a consequence of the small effective electron radii [23]. Exchange and correlation in the electron gas can be included by the Hubbard and Singwi-Sjölander schemes [24, 25].

The free-electron properties govern the electrical resistivity and the optical properties at least in the luminous and near-infrared spectral ranges; they are most conveniently discussed in terms of a complex dynamic resistivity, which is directly related to the dielectric function [26, 27]. From such an analysis it is clear that the ionized impurities are the dominant scattering centers, although grain boundary scattering can play some role in the mid-luminous spectral range. A general similarity between the theories for doped oxide semiconductor electrodes and for crystalline electrochromic tungsten oxide films should be noted [28].

The dc resistivity of the semiconductor-based transparent electrodes is of decisive influence for the dynamics of large-area electrochromic devices, and a minimum value is desirable. The magnitude of ϱ is governed by the ability to introduce dopant atoms, in most cases substitutionally, without creation of dopant-based absorbing aggregates. The electrical and optical properties of the films are dependent on the detailed deposition conditions, as discussed in a vast topical literature. The intention here is not to cover this literature in detail but merely to point at some key results and give references to representative work. For $In_2O_3:Sn$, that is most commonly used in electrochromic devices, films with $\varrho < 2 \times 10^{-4}\,\Omega\,\mathrm{cm}$ have been obtained by several different techniques such as reactive evaporation [8, 29–34], reactive sputtering [33–42], as well as chemical vapour deposition and spray pyrolysis [43–45]. The very lowest resistivities, $\varrho \leq 1 \times 10^{-4}\,\Omega\,\mathrm{cm}$, have been achieved by activated reactive evaporation and ion plating [46, 47] and by reactive rf magnetron sputtering [37]. Possibilities to lower ϱ by preconditioning of the $In_2O_3:Sn$ deposition material have been stressed [48]. Recent work indicates that an addition of Ge may minimize ϱ [49, 50].

Resistivities $< 2 \times 10^{-4}\,\Omega\,\mathrm{cm}$ have been reported also for ZnO:Al made by reactive sputtering [51, 52], $SnO_2:Sb$ made by activated reactive evaporation [53], $SnO_2:F$ made by spray pyrolysis [54], ZnO_x made by reactive evaporation [51, 55], InO_x made by coevaporation of In and In_2O_3 [56, 57], and $Cd_xSn_yO_2$ made by reactive sputtering [58, 59].

Optical data for optimized transparent electrodes based on heavily doped semiconductors can be computed quantitatively [8] from a theory that embraces the ideas outlined above. The theory is known [8] to yield results that are almost indistinguishable from experimental ones. Specifically, the theory includes three additive contributions: free-electron effects represented by n_e electrons per volume unit that undergo ionized impurity scattering against an equal density of positive charges according to the theory by Gerlach [27], valence-electron effects represented by a parameterization of the n_e-dependent bandgap widening, and phonon effects represented by a set of Lorentzian oscillators in basic agreement with bulk data [60]. Structural rearrangements due to dopant incorporation – which were verified in recent EXAFS data [61] on $In_2O_3:Sn$ – are not explicitly included. The only essential free parameter in the theory is n_e, which is related to the experimental value of ϱ. Further details on the application of this model to $In_2O_3:Sn$ and ZnO:Al are given in [8, 16].

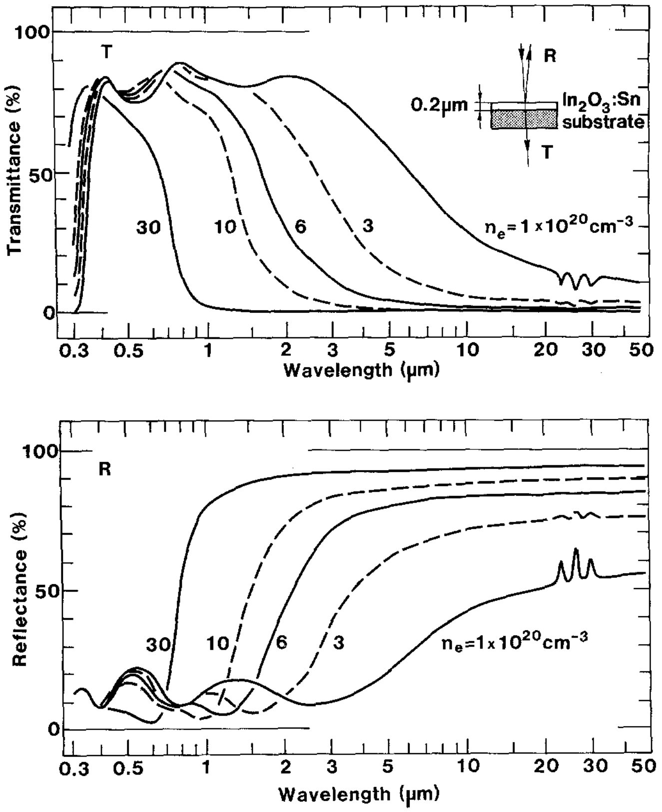

Fig. 1. Spectral normal transmittance T and reflectance R computed from a model for the optical properties of $In_2O_3:Sn$. The shown values of electron density n_e and film thickness were used. From Hamberg and Granqvist [8]

Figure 1 illustrates the computed transmittance and reflectance in the $0.3\,\mu\mathrm{m} < \lambda < 50\,\mu\mathrm{m}$ wavelength range and five n_e's for a $0.2\,\mu\mathrm{m}$ thick film described by parameters pertinent to $In_2O_3:Sn$. The film is backed by a substrate with a refractive index equal to 1.5. The film is transparent at short wavelengths and reflecting at long wavelengths; the crossover between those two regimes depends on n_e and occurs at a smaller wavelength the larger the electron density. The semiconductor bandgap at $\lambda < 0.4\,\mu\mathrm{m}$ shifts towards the ultraviolet as n_e goes up, and, at the same time, the phonon-induced structure at $20\,\mu\mathrm{m} < \lambda < 30\,\mu\mathrm{m}$ is washed out. At $n_e = 1 \times 10^{21}\,\mathrm{cm}^{-3}$, which is realized experimentally in $In_2O_3:Sn$ films with very low resistivity, the onset of high reflectance lies at $\sim 1\,\mu\mathrm{m}$. At $n_e = 3 \times 10^{21}\,\mathrm{cm}^{-3}$, theory predicts an onset of high reflectance at $\sim 0.7\,\mu\mathrm{m}$, but those high n_e's can not be reached in real samples because of the limitations on achievable doping levels.

It is found from Fig. 1 that an increase in n_e yielding a decrease in ϱ, has the effect of diminishing the transmittance T particularly in the infrared. In a practical electrochromic device – particularly one for modulating the solar energy throughput – there is a tradeoff situation, and an optimum n_e can be given. Figure 2 shows the computed dependence of the wavelength-integrated solar and luminous transmittance and reflectance (denoted T_{sol}, R_{sol}, T_{lum}, and R_{lum}, respectively) as a function of electron density for $In_2O_3:Sn$ films

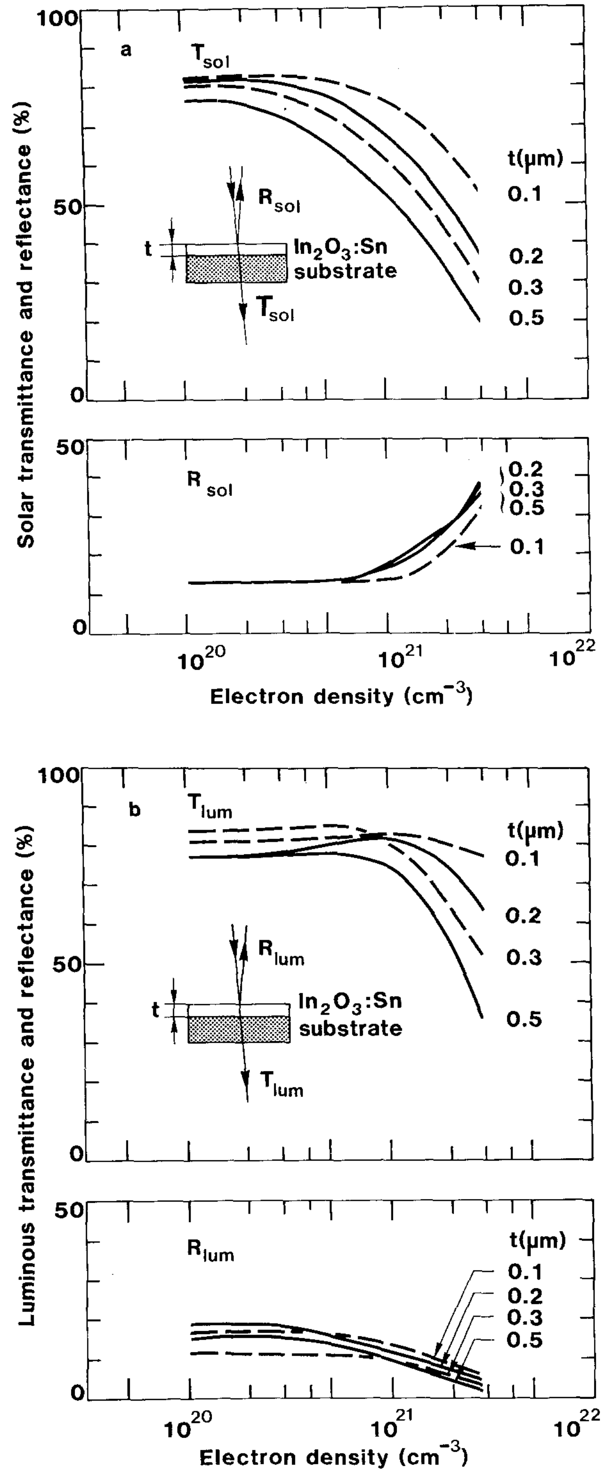

Fig. 2. Solar *(part a)* and luminous *(part b)* transmittance T and reflectance R vs electron density computed from a model for the optical properties of $In_2O_3:Sn$. Results are given for four film thicknesses t. From Hamberg and Granqvist [8]

with four thicknesses. T_{sol} is seen to drop sharply at high n_e's and to be as small as $\sim 54\%$ for a $0.5\,\mu m$ thick film with $n_e = 10^{21}\,cm^{-3}$. The transmittance limitation is caused mainly by absorption around the plasma wavelength, and the increase of R_{sol} is not as pronounced as the decrease of T_{sol}. For T_{lum}, the drop takes place only at $n_e > 10^{21} cm^{-3}$, which is understandable since the integration for the luminous properties is performed over shorter wavelengths than for the solar properties.

2 Thin Films of Coinage Metals

When coinage metal films are used as transparent electrodes, they need to be very thin in order to have a sizeable transmittance. The growth of thin metal films can be characterized in terms of a series of rather well defined stages, at least for films prepared by vapour deposition onto amorphous substrates [62, 63]. At the initial deposition, metallic nuclei are formed on the substrate surface. Continued deposition makes these nuclei grow via surface diffusion and direct impingement. The metal islands thus formed are mobile and undergo coalescence growth [64] so that larger and more irregular islands are formed. The growing film then passes through large-scale coalescence so that an extended metallic network is created. Subsequently the voids between the metallic paths become smaller and more regular, and finally a uniform metallic layer may be formed. It is obvious that metallic conduction is possible only for thicknesses exceeding the one where large scale coalescence takes place. The absolute thickness scale for the growth sequence depends on many parameters such as the deposited species, the presence of (artificially added) nucleation centers, the substrate temperature, vacuum conditions, the presence of electric fields, etc.

Figure 3 shows resistivity data for evaporated gold films, reproduced from van Attekum et al. [65], which serve as a convenient starting point for the discussion. For the as-deposited film, ϱ falls off sharply with increasing thickness and reaches an ultimate value of $\sim 3 \times 10^{-6}\,\Omega\,cm$ at large thickness irrespective of the substrate being silicon oxide or Pyrex glass. This resistivity is more than 25 times smaller than the lowest resistivity for the doped oxide

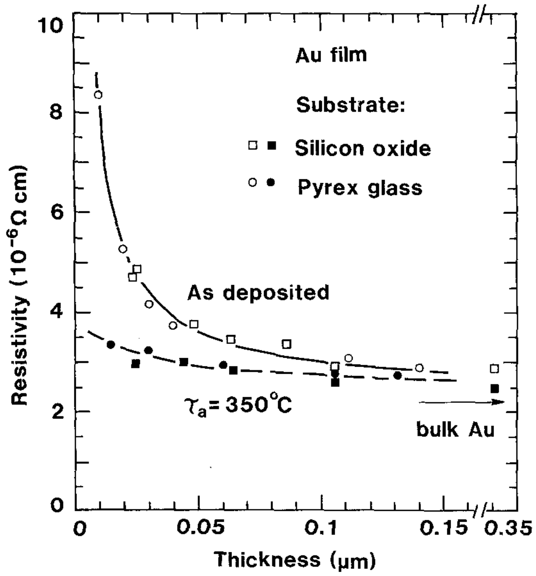

Fig. 3. Thickness-dependent electrical resistivity of gold films, evaporated onto two different substrates, in as-deposited state and after annealing at the shown temperature τ_a. The curves are drawn for convenience. An arrow indicates the resistivity of bulk Au. From van Attekum et al. [65]

semiconductors discussed in the previous section. After treatment of the gold films at 350° C for 15 min to 30 min, ϱ becomes significantly lower, especially at small thickness, and approaches the bulk value. Representative data, that are in principle agreement with those in Fig. 3, are given in [66, 67] and elsewhere.

Through extensive work it has been demonstrated that it is possible to lower ϱ at small thicknesses by deposition at a low substrate temperature [68], in the presence of a small amount of gas [69, 70], with an electric field along the substrate [71], by the application of inorganic or organic nucleation centers [3, 72, 73], and by bombarding the growing film by ions supplied either by an external source [74–76], inherently during sputtering [77], or by bias evaporation in conjunction with a partially ionized beam of impinging metal atoms [78]. An interesting technique, capable of giving patterned low-resistivity gold films, is focussed ion-beam irradiation of a substrate in contact with a gold-bearing gas such as $C_7H_7F_6O_2Au$ [79].

A very large amount of work has gone into theoretical modeling of the thickness-dependent metallic resistivity, but despite these efforts the situation is not yet fully clear. The major reasons for the resistivity increase in the thin-film limit are scattering against the external film boundaries and against its internal grain boundaries. For external boundary scattering, the theories are based on the semiclassical Boltzmann formalism [80, 81] or on quantum mechanical treatments using first-order perturbation schemes [82–85]. The results can be summarized by

$$\varrho = \varrho_\infty [1 + G(t^{-1}, cl_\infty)] , \tag{2}$$

where ϱ_∞ is the resistivity in the limit of infinite thickness and G is a function of inverse thickness and of the intrinsic scattering mean free path l_∞ times a constant c. In the semiclassical theory by Fuchs [80] and Sondheimer [81], c is $1 - p$, with p being a "specularity parameter", and in the quantum mechanical theory (in the limit of a continuous density of states for the metal) c can be identified with h^2, with h being the rms value of the microscopic roughness of the surface potential [82]. In practice, the applicability of the theory is limited by the existence of large-scale (mesoscopic) fluctuations of the local film thickness. After averaging the corresponding local resistivity over the entire film [84, 86, 87], it is possible to obtain an acceptable fit to experimental data [88]. Internal grain boundaries can also be of significance for the resistivity of thin metal films. As found from detailed investigations [66], this effect can be represented by an exponential dependence on l_∞ / D, with D being the average grain diameter. This dependence has been corroborated by quantum mechanical calculations [89]. In many other works on the conductivity of granular metals, the analysis is performed in terms of a semiclassical theory by Mayadas and Shatzkes [90].

Regarding optical transmittance through thin coinage metal films, silver is the superior material on account of its low luminous and solar absorptance [91, 92]. Gold and copper show absorption at $\lambda < 0.5\,\mu m$. TiN, which is noble-metal-like as regards the electronic properties, is similar to Au in its optical behaviour [93, 94]. Typical transmittance and reflectance data for very thin evaporated silver films are reported in Fig. 4, where results from Valkonen et al. [92] are replotted for the $0.35\,\mu m < \lambda < 16\,\mu m$ spectral range. At $t = 6\,nm$, the reflectance is low, indicating that the film consists of discrete islands. At $t \geq 9\,nm$, however, the reflectance shows a metallic behaviour. For these films the transmittance is $<55\%$ at $\lambda = 0.5\,\mu m$.

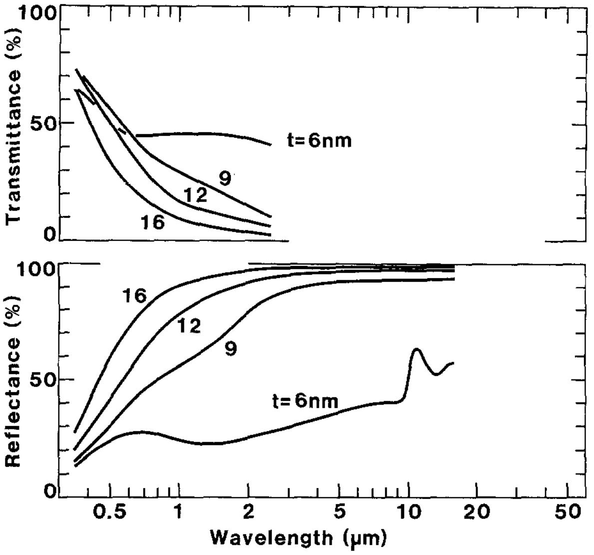

Fig. 4. Spectral transmittance and reflectance for silver films, having four different thicknesses t on glass substrates. After Valkonen et al. [92]

Figure 4 indicates that the transmittance is severely limited. If a metallic-like electrical conductivity is required, one is confined to $T_{lum} < 50\%$ and $T_{sol} < 40\%$ for films prepared by conventional evaporation [92]. By optimized ion-assisted evaporation or special sputter technology one can reach $T_{lum} \approx T_{sol} < 60\%$ [63, 77]. If an even higher transmittance is required, it is possible to use a multilayer coating including one or several dielectric layers, but such layers may, in some electrochromic devices, have the undesired effect of preventing ion permeation. The durability of silver based films can be significantly enhanced through the application of an additional metal layer (for example of Cu) [95]. A similar beneficial effect of Al has been noted for TiN-based films [96].

Theoretical models for the optical properties of extremely thin films must account for their non-homogeneous character. Such models are available for thicknesses well below large-scale coalescence [97–100], well above large-scale coalescence [63], and at the cross-over [101–103]. Except at cross-over, effective-medium-type theories [104] are appropriate for (semi)quantitative descriptions of the optical properties.

References

1. Z.M. Jarzebski, J.P. Marton: J. Electrochem. Soc. **123**, 199c, 299c, 333c (1976)
   Z.M. Jarzebski: Phys. Status Solidi A **71**, 13 (1982)
2. G. Haacke: Ann. Rev. Mater. Sci. **7**, 73 (1977)
3. J.L. Vossen: In *Physics of Thin Films*, ed. by G. Haas, M.H. Francombe, R.W. Hoffman, Vol. 9 (Academic, New York 1977) p. 1
4. H. Köstlin: Festkörperprobleme **22**, 229 (1982)
5. J.C. Manifacier: Thin Solid Films **90**, 297 (1982)
6. P.H. Berning: Appl. Opt. **22**, 4127 (1983)

7. K.L. Chopra, S. Major, K. Pandya: Thin Solid Films **102**, 1 (1983)
8. I. Hamberg, C.G. Granqvist: J. Appl. Phys. **60**, R123 (1986)
9. C.G. Granqvist: *Spectrally Selective Surfaces for Heating and Cooling Applications* (SPIE Opt. Eng. Press, Bellingham, USA 1989)
10. C.G. Granqvist: In *Electricity: Efficient End-use and New Generation Technologies, and Their Planning Implications*, ed. by T.B. Johansson, B. Bodlund, R.H. Williams (Lund University Press, Lund, Sweden 1989) p. 89
11. C.G. Granqvist: Appl. Phys. A **52**, 83 (1991)
12. C.G. Granqvist: In *Materials Science for Solar Energy Conversion Systems*, ed. by C.G. Granqvist (Pergamon, Oxford, UK 1991) p. 106
13. R. Furler, P. Williams, F.K. Kneubühl: Infrared Phys. **33**, 321 (1992)
14. N.R. Lynam: In *Proc. Symp. Electrochromic Materials*, ed. by M.K. Carpenter, D.A. Corrigan (The Electrochem. Soc., Pennington 1990) Proc. Vol. 90-2, p. 201
15. M. Misonou, H. Kawahara: In *Large-area Chromogenics: Materials and Devices for Transmittance Control*, ed. by C.M. Lampert, C.G. Granqvist (SPIE Opt. Eng. Press, Bellingham, USA 1990) p. 402
16. Z.-C. Jin, I. Hamberg, C.G. Granqvist: J. Appl. Phys. **64**, 5117 (1988)
17. J.J.P. Elich, E.C. Boslooper, H. Haitjema: Thin Solid Films **177**, 17 (1989)
    H. Haitjema, J.J.P. Elich, C.J. Hoogendoorn: Solar Energy Mater. **18**, 283 (1989)
18. J.R. Bellingham, W.A. Phillips, C.J. Adkins: J. Mater. Sci. Lett. **11**, 263 (1992)
19. B.E. Sernelius: Thin Solid Films **208**, 96 (1992)
20. Y. Shigesato, Y. Hayashi, T. Haranoh: Appl. Phys. Lett. **61**, 73 (1992)
21. B. Stjerna, C.G. Granqvist: Proc. SPIE **1272**, 12 (1990); Thin Solid Films **193/194**, 704 (1990); Appl. Phys. Lett. **57**, 1989 (1990)
    B. Stjerna, C.G. Granqvist, A. Seidel, L. Häggström: J. Appl. Phys. **68**, 6241 (1990)
22. J. Lindhard: K. Dan. Vidensk. Selsk. Mat. Fys. Medd. **28** (8) (1954)
23. G. Mahan: *Many Particle Physics* (Plenum, New York 1981)
24. J. Hubbard: Proc. Roy. Soc. (London) A **243**, 336 (1957)
25. K.S. Singwi, M.P. Tosi, R.H. Land, A. Sjölander: Phys. Rev. **176**, 589 (1968)
    P. Vashishta, K.S. Singwi: Phys. Rev. B **6**, 875 (1972)
26. M.G. Calkin, P.J. Nicholson: Rev. Mod. Phys. **39**, 361 (1967)
27. E. Gerlach, P. Grosse: Festkörperprobleme **17**, 157 (1977)
    E. Gerlach: J. Phys. C **19**, 4585 (1986)
28. J.S.E.M. Svensson, C.G. Granqvist: Appl. Phys. Lett. **45**, 828 (1984)
29. M. Mizuhashi: Thin Solid Films **70**, 91 (1980)
30. Z. Ovadyahu, B. Ovryn, K.W. Kraner: J. Electrochem. Soc. **130**, 917 (1983)
31. Y. Cui, X. Xu, Z. Jin, C. Peng, S. Xie: Thin Solid Films **115**, 195 (1984)
32. S.-W. Jan, S.-C. Lee: J. Electrochem. Soc. **134**, 2056 (1987)
33. Y. Shigesato: Jpn. J. Appl. Phys. **30**, 1457 (1991)
34. Y. Shigesato, S. Takaki, T. Haranoh: J. Appl. Phys. **71**, 3356 (1992)
35. D.B. Fraser, H.D. Cook: J. Electrochem. Soc. **119**,1368 (1972)
36. S. Maniv, C.J. Miner, W.D. Westwood: J. Vac. Sci. Technol. A **1**, 1370 (1983)
37. S. Ray, R. Banerjee, N. Basu, A.K. Batabyal, A.K. Barna: J. Appl. Phys. **54**, 3497 (1983)
38. S. Yamamoto, T. Yamanaka, Z. Ueda: J. Vac. Sci. Technol. A **5**, 1952 (1987)
39. H. Nanto, T. Minami, S. Orito, S. Takata: J. Appl. Phys. **63**, 2711 (1988)
40. T. Minami, H. Sato, H. Nanto, S. Takata: Thin Solid Films **176**, 277 (1989)
41. S. Ray, J. Dutta, A.K. Barua, S.K. Deb: Thin Solid Films **199**, 201 (1991)
42. M.A. Martinez, J. Herrero, M.T. Gutierrez: Solar Energy Mater. Solar Cells **26**, 309 (1992)
43. G. Frank, H. Köstlin: Appl. Phys. A **27**, 197 (1982)
44. L.A. Ryabova, V.S. Salun, I.A. Serbinov: Thin Solid Films **92**, 327 (1982)
45. T. Maruyama, K. Fukui: J. Appl. Phys. **70**, 3848 (1991)
46. P. Nath, R.F. Bunshah: Thin Solid Films **69**, 63 (1980)
    P. Nath, R.F. Bunshah, B.M. Basol, O.M. Staffsud: Thin Solid Films **72**, 463 (1980)
47. S. Takaki, K. Matsumoto, K. Suzuki: Appl. Surf. Sci. **33/34**, 919 (1988)
48. M. Mizuhashi, K. Suzuki, S. Takagi: Jpn. Patent Appl. 63-199862 (1988)
49. S.J. Wen, G. Campet, J. Portier, G. Couturier, J.B. Goodenough: Mater. Sci. Engr. B **14**, 115 (1992)
50. Y. Xu, J. Salardenne, S. Wen, G. Campet, T. Buffeteau, B. Desbat: ISSI Lett. **3**, 7 (1992)
51. T. Minami, H. Nanto, S. Takata: Jpn. J. Appl. Phys. **23**, L280 (1984)
    T. Minami, H. Sato, H. Nanto, S. Takata: Jpn. Appl. Phys. **24**, L781 (1985)
    S. Takata, T. Minami, H. Nanto: Thin Solid Films **135**, 183 (1986)
52. Y. Igasaki, M. Ishikawa, G. Shimaoka: Appl. Surf. Sci. **33/34**, 926 (1988)
    Y. Igasaki, H. Saito: J. Appl. Phys. **69**, 2190 (1991); **70**, 3613 (1991)
53. H.S. Randhawa, M.D. Matthews, R.F. Bunshah: Thin Solid Films **83**, 267 (1981)
54. C. Agashe, B.R. Marathe, M.G. Takwale, V.G. Bhide: Thin Solid Films **164**, 261 (1988)
55. H. Nanto, T. Minami, S. Shooji, S. Takata: J. Appl. Phys. **55**, 1029 (1984)
56. C.A. Pan, T.P. Ma: Appl. Phys. Lett. **37**, 163 (1980); J. Electronic Mater. **10**, 43 (1981); J. Electrochem. Soc. **128**, 1953 (1981)
57. J.R. Bellingham, W.A. Phillips, C.J. Adkins: Thin Solid Films **195**, 23 (1991)
58. G. Haacke: Appl. Phys. Lett. **28**, 622 (1976)
59. N. Miyata, K. Miyaka, Y. Yamaguchi: Appl. Phys. Lett. **37**, 180 (1980)
60. W.B. White, V.G. Keramidas: Spectrochim. Acta A**28**, 501 (1972)
61. P. Parent, H. Dexpert, G. Tourillon, J.-M. Grimal: J. Electrochem. Soc. **139**, 276, 282 (1992)
62. K.L. Chopra: *Thin Film Phenomena* (McGraw-Hill, New York 1969)
63. G.B. Smith, G.A. Niklasson, J.S.E.M. Svensson, C.G. Granqvist: J. Appl. Phys. **59**, 571 (1986)
64. J.R. Levine, J.B. Cohen, Y.W. Chung: Surf. Sci. **248**, 215 (1991)
65. P.M.T.M. van Attekum, P.H. Woerlee, G.C. Verkade, A.A.M. Hoeben: Phys. Rev. B **29**, 645 (1984)
66. H. Hoffmann, J. Vancea: Thin Solid Films **85**, 147 (1981)
    H. Hoffmann: Festkörperprobleme **22**, 255 (1982)
    J. Vancea, H. Hoffmann: Thin Solid Films **92**, 219 (1982)
    J. Vancea, H. Hoffmann, K. Kastner: Thin Solid Films **121**, 201 (1984)
67. J.R. Sambles, K.C. Elsom, D.J. Jarvis: Philos. Trans. R. Soc. (London) A **304**, 365 (1982)
68. W. Schlemminger, D. Stark: Thin Solid Films **137**, 49 (1986)
69. G.C. Paulson, A.L. Friedberg: Thin Solid Films **5**, 47 (1970)
70. V.D. Frechette, J.C. Pulver, D.R. Rossington: J. Am. Ceram. Soc. **64**, 463 (1981)
71. T.G. Andersson: J. Phys. D **9**, 973 (1976)
72. H.K. Chaurasia, W.A.G. Voss: Nature **249**, 28 (1974)
73. D.L. Allara, A.F. Hebard, F.J. Padden, R.G. Nuzzo, D.R. Falcone: J. Vac. Sci. Technol. A **1**, 376 (1983)
74. S.S. Nandra, F.G. Wilson, C.D. DesForges: Thin Solid Films **107**, 335 (1983)
75. P.J. Martin, R.P. Netterfield: In *Progress in Optics* (Elsevier, Amsterdam 1986) Vol. XXIII, p. 113
    P.J. Martin: J. Mater. Sci. **21**, 1 (1988)
76. N. Savvides: Thin Solid Films **163**, 13 (1988)
77. E. Valkonen, C.-G. Ribbing: Mater. Lett. **3**, 29 (1984)
78. P. Bai, G.-R. Yang, T.-M. Lu: Appl. Phys. Lett. **56**, 198 (1990)

79. P.G. Blauner, Y. Butt, J.S. Ro, C.V. Thompson, J. Melngailis: J. Vac. Sci. Technol. B **7**, 1816 (1989)
80. K. Fuchs: Proc. Cambridge Philos. Soc. **34**, 100 (1938)
81. E.H. Sondheimer: Adv. Phys. **1**, 1 (1952)
82. Z. Tesanović, M.V. Jarić, S. Mackawa: Phys. Rev. Lett. **57**, 2760 (1986)
Z. Tesanović: J. Phys. C **20**, L829 (1987)
83. C.S. Chu, R.S. Sorbello: Phys. Rev. B **38**, 7260 (1988)
84. N. Trivedi, N.W. Ashcroft: Phys. Rev. B **38**, 12298 (1988)
85. G. Fishman, D. Calecki: Phys. Rev. Lett. **62**, 1302 (1989)
D. Calecki, G. Fishman: Surf. Sci. **229**, 110 (1990)
86. Y. Namba: Jpn. J. Appl. Phys. **9**, 1326 (1970)
87. U. Jacob, J. Vancea, H. Hoffmann: Phys. Rev. B **41**, 11852 (1990)
G. Reiss, E. Hastreiter, H. Brückl, J. Vancea: Phys. Rev. B **43**, 5176 (1991)
88. J. Vancea, G. Reiss, H. Hoffmann: J. Mater. Sci. Lett. **6**, 985 (1987)
J. Vancea: Int. J. Mod. Phys. B **3**, 1455 (1989)
89. G. Reiss, J. Vancea, H. Hoffmann: Phys. Rev. Lett. **56**, 2100 (1986)
90. A.F. Mayadas, M. Shatzkes: Phys. Rev. B **1**, 1382 (1970)
91. J.C.C. Fan, F.J. Bachner: Appl. Opt. **15**, 1012 (1976)
92. E. Valkonen, B. Karlsson, C.-G. Ribbing: Solar Energy **32**, 211 (1984)
E. Valkonen, B. Karlsson: Energy Res. **11**, 397 (1987)
93. C.-G. Ribbing, E. Valkonen: Proc. SPIE **652**, 166 (1986)
E. Valkonen, C.-G. Ribbing, J.-E. Sundgren: Proc. SPIE **652**, 235 (1986)
Y. Claesson, M. Georgson, A. Roos, C.-G. Ribbing: Solar Energy Mater. **20**, 455 (1990)
A. Skerlavaj, Y. Claesson, C.-G. Ribbing: Thin Solid Films **186**, 15 (1990)
94. A.G. Spencer, M. Georgson, C.A. Bishop, E. Stenberg, R.P. Howson: Solar Energy Mater. **18**, 87 (1988)
95. K. Chiba, K. Suzuki: Solar Energy Mater. Solar Cells **25**, 113 (1992)
96. K.E. Andersson, M.K. Wahlström, A. Roos: Thin Solid Films **214**, 213 (1992)
97. S. Norrman, T. Andersson, C.G. Granqvist, O. Hunderi: Phys. Rev. B **18**, 674 (1978)
98. J. Vlieger, D. Bedeaux: Thin Solid Films **69**, 107 (1980)
D. Bedeaux, J. Vlieger: Thin Solid Films **102**, 265 (1983)
P.A. Bobbert, J. Vlieger: Physica A **137**, 209 (1986); Physica A **147**, 115 (1987)
P.A. Bobbert, J. Vlieger, R. Greef: Physica A **137**, 243 (1986); Thin Solid Films **164**, 63 (1988)
M.M. Wind, J. Vlieger, D. Bedeaux: Physica A **141**, 33 (1987)
M.M. Wind, P.A. Bobbert, J. Vlieger, D. Bedeaux: Physica A **143**, 164 (1987); Thin Solid Films **164**, 57 (1988)
99. G.A. Niklasson, H.G. Craighead: Thin Solid Films **125**, 165 (1985)
100. N. Stefanou, A. Modinos: J. Phys. Cond. Matter. **3**, 8135, 8149 (1991)
A. Modinos, N. Stefanou: Acta Phys. Pol. A **81**, 91 (1992)
101. P. Gadenne, A. Beghdadi, J. Lafait: Opt. Commun. **65**, 17 (1988)
M. Gadenne, J. Lafait, P. Gadenne: Opt. Commun. **71**, 273 (1989)
102. Y. Yagil, G. Deutscher: Appl. Phys. Lett. **52**, 373 (1988)
Y. Yagil, M. Yosefin, D.J. Bergman, G. Deutscher, P. Gadenne: Phys. Rev. B **43**, 11342 (1991)
103. C.A. Davis, D.R. McKenzie, R.C. McPhedran: Opt. Commun. **85**, 70 (1991)
104. G.A. Niklasson: In *Materials Science for Solar Energy Conversion Systems*, ed. by C.G. Granqvist (Pergamon, Oxford, UK 1991) p. 7