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Highly conductive and transparent amorphous tin oxide

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The physical properties of chemically sprayed tin oxide films have been investigated. The optical and transport behavior of both amorphous and polycrystalline material depends on the reaction temperature. Amorphous films deposited at very low temperatures ($T_s = 220^\circ\text{C}$) possess a conductivity as high as that of the polycrystalline layers. Hall effect measurements and compositional analyses of those amorphous films show that nonintentional chlorine doping is responsible for the increased conductivity. Optical transmission in the visible region of the spectrum is almost as good in amorphous as in polycrystalline material. An antireflecting coating of amorphous tin oxide with an optical gain of 40% has been achieved on silicon wafers. Furthermore, film thickness homogeneity broadens the field of application to various optoelectronic devices.

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Tin oxide films are widely used as transparent electrodes on glass substrates and as antireflecting coatings on solar cells because of their high electrical conductivity combined with low absorption in the visible spectrum. The physical properties of polycrystalline films have been largely investigated in the last two decades. A complete review on the matter has been given by Jarzebski and Marton¹ in 1976. On the contrary and somewhat in contrast with the growing interest in low-temperature technologies for solar cell fabrication, studies on the physical properties of amorphous tin oxide films are still missing. In view of its simplicity the chemical spray method appears to be one of the most suitable among the various preparation techniques. *n*-type conductivity always found in nonintentionally doped films has been attributed to deviations from stoichiometry, i.e., oxygen vacancies or interstitial tin. Moreover, halogen atoms are also doping agents in tin oxide.^{2,3} Recently, Chambouleyron *et al.*⁴ have estimated to a few atomic percent the chlorine content in the films deposited by the spray method at low temperatures. In a recent paper⁵ we have shown that films deposited at temperatures lower than 300°C are amorphous. The purpose of the present study is to investigate the properties of films fabricated by the spray method at temperatures as low as 220°C .

Our tin oxide films were prepared by spraying an alcohol solution of stannic chloride on glass substrates held at temperatures ranging between 220° and 520°C . The experimental setup has been previously described.⁴ All samples with thickness ranging from 0.5 to $1.1\ \mu\text{m}$ were obtained from an identical spray solution consisting of 1.75 g of SnCl_4 , 5 H_2O diluted in 25 ml of pure ethanol. Nitrogen flowing at 7 l/min was used as the carrier gas and the spray rate was 1 ml/min. The substrate temperature T_s was continuously monitored by a chromel-alumel thermocouple fixed on the top surface of the substrate. The absolute uncertainty of T_s was $\pm 10^\circ\text{C}$ and temperature fluctuations during deposition were maintained within $\pm 5^\circ\text{C}$.

The amorphous or polycrystalline structure of the film

was verified by x-ray diffraction. Film thickness, refractive index, and absorption coefficient at low photon energies (1.3–2.5 eV) were deduced from transmission interference patterns⁶ using either a Beckman DK 2A or a Zeiss DMC 25 spectrophotometer. On the same films we measured the electrical conductivity and Hall coefficient R_H by the Van der Pauw's technique.

We have performed mechanical Talystep measurements in order to estimate the surface roughness of the films (Fig. 1). Polycrystalline films present a high surface roughness of the order of the film thickness. For some applications such as antireflecting coatings on solar cells this is not a serious problem. On the contrary amorphous films have a surface roughness of less than $500\ \text{\AA}$ which allows the use of this material as an electrode deposited on glass in a large scale of applications such as vidicon and optoelectronic devices.

Hall measurements show that both amorphous and polycrystalline materials are degenerate *n*-type semiconductors. In amorphous films no Hall constant sign anomaly was observed in contrast to other amorphous semiconductors such as amorphous silicon⁷ or III-V compounds.⁸ This result was somewhat expected because the classical Hall treatment applies to degenerate amorphous semiconductors.⁹ Figure 2 shows the variations of room temperature conductivity, electron concentration N , and electron Hall mobility μ as a function of substrate temperature. N has been calculated from the classical formula $R_H = -r/qN$ assuming a scattering Hall coefficient r equal to unity.

A three orders of magnitude decrease in conductivity is observed at the crystalline-amorphous transition temperature ($\sim 300^\circ\text{C}$). This large discontinuity results from a one order of magnitude change in mobility and a two orders of magnitude change in electron concentration.

On the polycrystalline side, the highest μ values of $10\text{--}15\ \text{cm}^2\ \text{V}^{-1}\ \text{s}^{-1}$ are obtained for $300^\circ\text{C} < T_s < 400^\circ\text{C}$. In this temperature range N values are much higher than the degeneracy limit of $\sim 5 \times 10^{18}\ \text{cm}^{-3}$ that we assumed for crystalline tin oxide.⁵ The mobility nearly follows a $1/N$ dependence which leads to a $130(\Omega\ \text{cm})^{-1}$ plateau of conductivity. At deposition temperatures higher than 400°C , the

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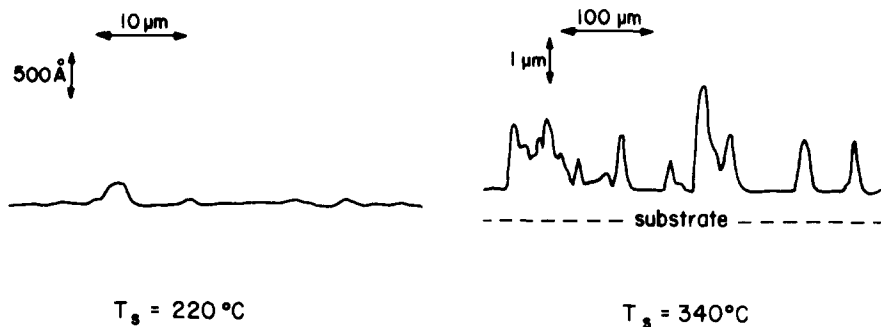


FIG. 1. Mechanical Talystep measurement on surfaces of amorphous ($T_s = 220^\circ\text{C}$) and polycrystalline ($T_s = 340^\circ\text{C}$) films.

low mobility values measured in this region are probably due to grain boundary scattering which has been found to be the dominant scattering mechanism limiting the mobility for tin oxide films prepared at high temperature.¹⁰

On the amorphous side the measured μ values are consistent with those expected for electron conduction through extended states. Assuming that the classical Hall treatment applies, the Hall mobility would be equal to the conductivity mobility μ_c . In first approximation μ_c is given by the Cohen's formula for Brownian-type motion¹¹ $\mu_c = ea^2\nu_{el}/6kT$ where e is the electronic charge, a the interatomic distance, and ν_{el} the electronic frequency ($\sim 10^{15} \text{ s}^{-1}$). One finds at room temperature $\mu_c = 2.5 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ with $a = 2 \text{ \AA}$. Experimental values range between 0.5 and $2 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. However, in the presence of a high concentration of impurity atoms as we shall discuss later, impurity band conduction may lead to slightly lower mobility values.

One interesting point is the marked influence of substrate temperature on carrier concentration in amorphous tin oxide (Fig. 2). A value of $N = 3 \times 10^{20} \text{ cm}^{-3}$ has been obtained for $T_s = 220^\circ\text{C}$. Smoother variations are obtained when T_s is lowered from 520° to 300°C in the polycrystalline

region. When reaction temperatures are lower than 500°C the incomplete hydrolysis of stannic chloride is presumed to liberate atomic oxygen, hydrogen, and chlorine.¹² These elements will partially fill oxygen vacancies and chlorine has been suggested to be the doping agent of chemically sprayed tin oxide films but no proof of it has been given yet. In order to clarify this point, we have attempted a correlation between our N values and results of SIMS and AES compositional analyses.⁴ The impurities detected were chlorine, hydrogen, and OH groups. Quantitative determination of the impurity concentration was only possible for the chlorine content which is represented in Fig. 3 as a function of inverse substrate temperature. In contrast to chlorine concentration, hydrogen and OH concentration appeared to be independent of the deposition temperature of the films but no absolute values could be deduced. We have plotted also on Fig. 3 the variations of the electron concentrations taken from Fig. 2. The correlation is fairly good with some peculiarities concerning the chlorine doping efficiency. Chlorine introduces a single donor level and our results show that for $T_s \sim 400^\circ\text{C}$ the concentration of chlorine impurities is nearly equal to the free electron concentration. This is consistent

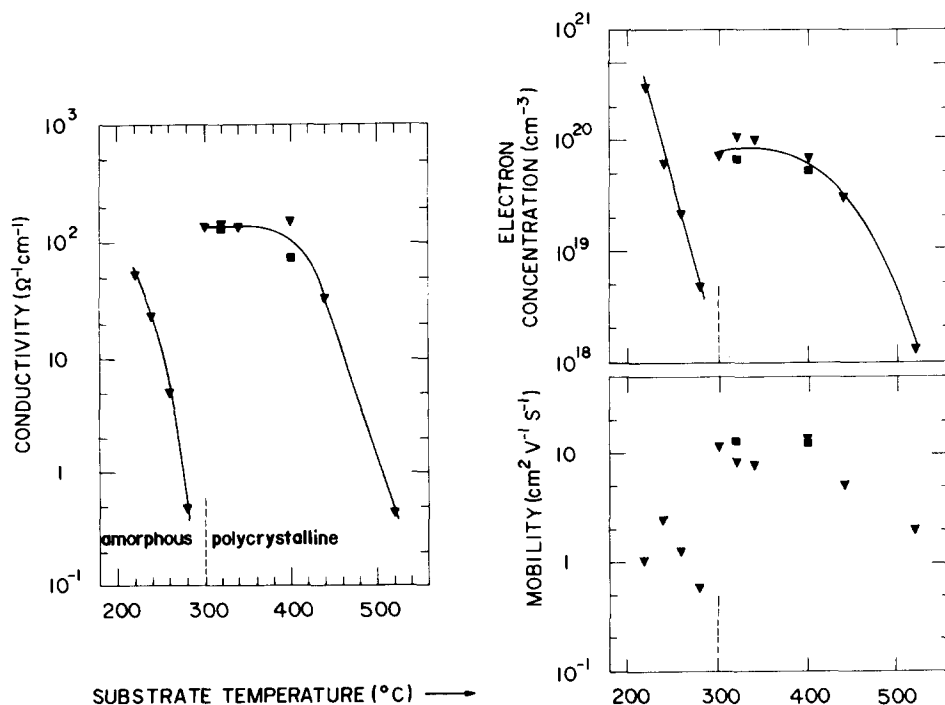


FIG. 2. Variations of room temperature conductivity, electron Hall mobility, and carrier concentration as a function of substrate temperature (solution fluxes: \blacktriangledown 1 ml/min, \blacksquare 4 ml/min).

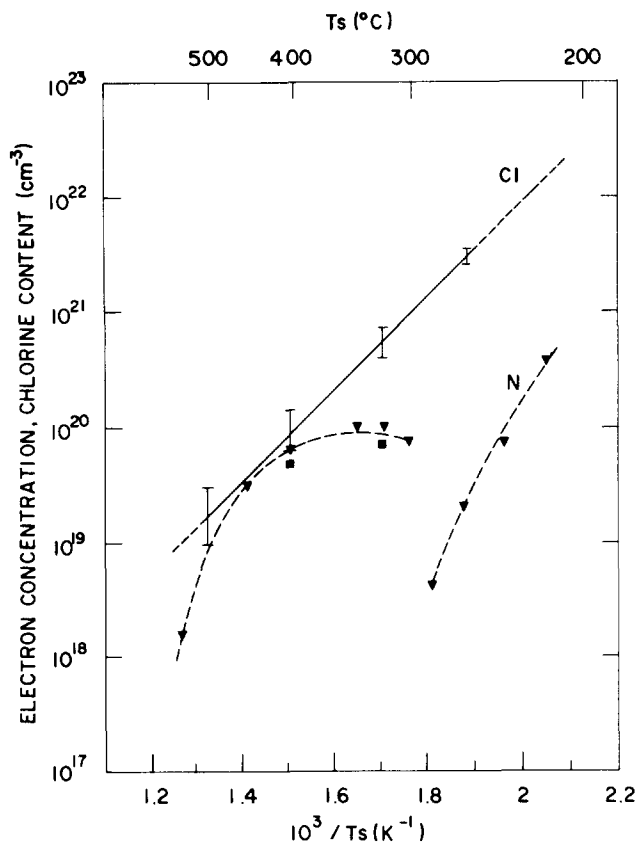


FIG. 3. Electron concentration and chlorine content (from Ref. 4) plotted as a function of inverse substrate temperature.

with a chlorine doping having nearly 100% efficiency. At all other temperatures the chlorine content is much higher than the measured free electron concentration. This clearly indicates that not all chlorine atoms included in the lattice behave as active donors. At high substrate temperature ($T_s > 400^\circ\text{C}$) we suggest that alkali ions from the glass substrate are diffusing into the film as has been reported for various transparent semiconductors.¹³ The elements of very small ionic radii such as L_i^+ and N_a^+ can fit easily into substitutional sites and behave as acceptors, thus leading to a compensating effect of chlorine doping. The very low chlorine doping efficiency ($\sim 1\%$) in amorphous tin oxide may be explained by three cumulative effects: (i) the existence of electronic states in the forbidden gap due to disorder and structural defects delays the Fermi level shift with increasing donor concentration; (ii) a significant part of chlorine atoms might contribute to the passivation of structural defects in atomic configurations where they behave as electrically inactive centers; (iii) the compensation effect of the simultaneous creation of acceptor states. In the latter case, the nature of the compensating centers is uncertain at this point. As the temperature is lowered, the combination of the three effects would lead to an increase of the doping efficiency as experimentally observed: 0.3% at 280°C and 3% at 220°C . The results in the intermediate range of substrate temperatures ($300^\circ\text{--}400^\circ\text{C}$) are not easy to interpret. We suggest that near the crystalline-amorphous transition a composite mate-

TABLE I. Optical parameters of tin oxide layers.

| | Thickness (\AA) | Refractive index at $\lambda = 0.65 \mu\text{m}$ | Mean transmission in the visible spectrum (film + substrate) |
|--|----------------------------|--|--|
| Amorphous $T_s = 220^\circ\text{C}$ | 4800 | 1.89 | 74% |
| Polycrystalline $T_s = 340^\circ\text{C}$ | 6700 | 1.84 | 81% |

rial of both phases is deposited which would explain the reduced doping efficiency. According to classical percolation theory, our electrical measurements would indicate that the composite material is at least 15% rich in polycrystalline phase.

Optical transparency of tin oxide is generally required in the visible and the near-infrared region. The transmission curves as a function of incident wavelength λ in the $0.4\text{--}1.1 \mu\text{m}$ range are given for two films, one amorphous and one polycrystalline, deposited on glass substrates at 220° and 340°C , respectively. Film thickness and refractive index are mentioned in Table I as well as the mean transmission in the visible spectrum calculated with the data of Fig. 4. For $\lambda > 0.6 \mu\text{m}$, the absorption coefficient α shows a low-energy tail of absorption with α nearly constant with photon energy ($\alpha \sim 10^3 \text{ cm}^{-1}$) and equal transmission for the two films. On the contrary, α shows an exponential type dependence on photon energy near the fundamental absorption edge⁵ which is shifted from $\lambda = 0.3 \mu\text{m}$ (polycrystalline) to $\lambda = 0.6 \mu\text{m}$ (amorphous).

At first glance, the measured transmission loss in amorphous films in the $0.3\text{--}0.6 \mu\text{m}$ range of wavelength would be disadvantageous. In fact required film thickness for an anti-reflecting coating on solar cells is about 750 \AA as illustrated in Fig. 5, where we show the reflectance curves of a 111-oriented silicon substrate before and after the deposition of a 750-\AA thick amorphous layer ($T_s = 220^\circ\text{C}$). For such a film

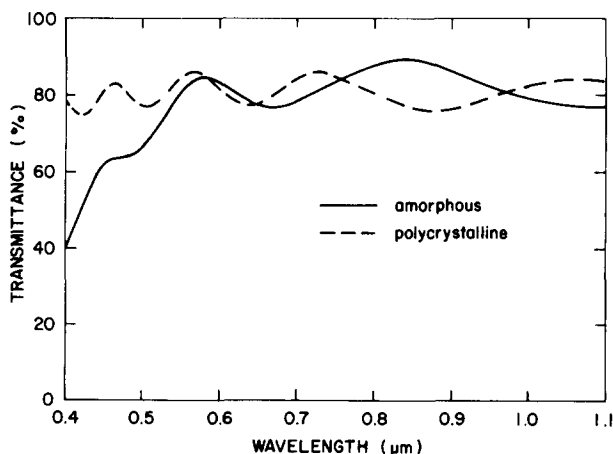


FIG. 4. Transmission curves vs incident wavelength in the range $0.4\text{--}1.1 \mu\text{m}$, full line: amorphous layer $T_s = 220^\circ\text{C}$, dashed line: polycrystalline layer $T_s = 340^\circ\text{C}$.

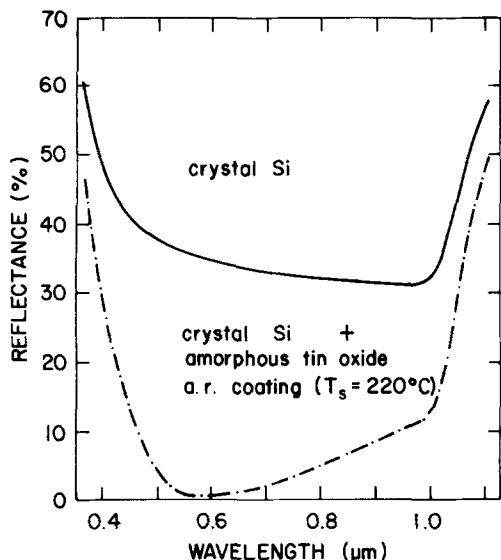


FIG. 5. Reflectance vs incident wavelength of a 111-silicon substrate before and after the deposition of an amorphous tin oxide antireflecting coating.

a simple calculation shows that the mean transmission remains higher than 90%. The loss in number of photons is only about 2% when a 220 °C amorphous film is used instead of a 340 °C polycrystalline one. The optical gain of 40% calculated from Fig. 5 compares very well with that typically obtained for polycrystalline films deposited at 350°– 450 °C.

Furthermore, low-temperature deposited films have been shown to produce an additional increase in photocurrent of *p/n* junctions.¹⁴ This has been interpreted as a passivation of silicon surface recombination centers most probably by hydrogen atoms¹⁵ produced by the incomplete hydrolysis reaction.

In conclusion, the high conductivity and good transpar-

ency of amorphous tin oxide films combined with passivation effects of semiconductor surfaces make this new material highly recommended particularly for photovoltaic applications. The flat morphology of the film surface allows a larger field of applications in electronic devices. The very low temperature for deposition required matches well with amorphous silicon technology.

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