

Optimization of Transparent and Reflecting Electrodes for Amorphous Silicon Solar Cells

Annual Technical Report,
1 April 1995 - 31 March 1996

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A national laboratory of
the U.S. Department of Energy
Managed by Midwest Research Institute
for the U.S. Department of Energy
under Contract No. DE-AC36-83CH10093

Prepared under Subcontract No. XAN-4-11318-05

August 1996

Preface

This report presents results obtained during the second year of a three-year phased subcontract from the National Renewable Energy Laboratory. (a national laboratory of the U. S. Department of Energy, operated by the Midwest Research Institute) to Harvard University (subcontract number XAN-4-11318-05 to the prime contract DE-AC02-83CH10093). The research was carried out under the direction of Roy G. Gordon, Professor of Chemistry and Chairman of the Department of Chemistry at Harvard University. Graduate student John Thornton prepared the chemical precursors used. Post-doctoral fellow Hirotoishi Sato was responsible for deposition of fluorine-doped zinc oxide films and measurements of their properties. Graduate student Haifan Liang prepared the doped titanium dioxide films and measured their properties. Solar cells were deposited on some of these films and tested by Team member Steven Hegedus at the Institute for Energy Conversion at the University of Delaware, and Subhendu Guha at United Solar Systems.

Executive Summary

Summary of Objectives

The general objective is to develop methods to deposit materials which can be used to make more efficient solar cells. The work is organized into three general tasks:

Task 1. Develop improved methods for depositing and using transparent conductors of fluorine-doped zinc oxide in amorphous silicon solar cells

Task 2. Deposit and evaluate titanium oxide as a reflection-enhancing diffusion barrier between amorphous silicon and an aluminum or silver back-reflector.

Task 3. Deposit and evaluate electrically conductive titanium oxide as a transparent conducting layer on which more efficient and more stable superstrate cells can be deposited.

About one-third of the current project resources are allocated to each of these three objectives.

An amorphous silicon solar cell incorporating these new materials will have the following structure:

glass
ZnO:F
TiO ₂ :Nb
p-uc Si
i-a Si
n-uc Si
TiO ₂ :Nb
ZnO:F
Al or Ag

Fluorine-doped Zinc Oxide (ZnO:F)

Solar cells need a transparent, electrically conductive front-surface electrode. We demonstrated that fluorine-doped zinc oxide is the most transparent conductor, for a given electrical sheet resistance, of any known material. We showed how to deposit it by low-cost, high-productivity

chemical vapor deposition at atmospheric pressure (APCVD). However, ZnO:F has not yet been used in commercial solar cells because the APCVD process was not reproducible enough, and used a hazardous (pyrophoric) zinc precursor.

We identified a non-hazardous zinc precursor, and showed that it could be used in a reproducible APCVD process to produce transparent, electrically conductive ZnO:F films over small areas of glass. We also found that a barrier material was needed between soda-lime glass and fluorine-doped zinc oxide made by this CVD reaction. Amorphous aluminum oxide (alumina) was identified as the best material for this barrier. Small areas of alumina film were prepared by a spray process in order to test the performance of this material as a barrier. An APCVD process is now under development for preparing the necessary larger areas of alumina films. During the next contract period, we expect to complete the scaling up of both the alumina and ZnO:F processes.

Back Reflectors

A transparent, electrically conductive diffusion barrier is needed between amorphous silicon and the back metal electrode (silver or aluminum). Aluminum-doped zinc oxide is usually employed to form this diffusion barrier. However, the reflectivity of this conventional back contact is lower than expected theoretically, perhaps because of diffusion of silver into the zinc oxide.

During this phase of the contract, we tested the properties of titanium oxide as a possible replacement for zinc oxide. Titanium oxide has a more densely packed crystal structure than zinc oxide, and thus it may be a better diffusion barrier than zinc oxide. We found that a titanium dioxide layer could be inserted over the metal back-reflector without loss of optical or electrical characteristics, but a gain in cell stability or efficiency has not yet been demonstrated.

Titanium Dioxide Diffusion Barriers

Micro-crystalline p-Si layers are known to produce more efficient solar cells than amorphous p-Si layers. Unfortunately, the conditions which deposit micro-crystalline p-Si layers destroy the usual transparent conductors (either tin oxide or zinc oxide). Research under the previous phase of this contract showed that niobium-doped titanium dioxide is a more stable transparent conductor.

Thin niobium-doped titanium dioxide films were deposited on top of tin oxide films, and were found to protect the tin oxide against chemical etchants. These bilayer films were also used as substrates for growing amorphous silicon solar cells. These cells had normal voltages and fill factors, but lower currents, because of some optical absorption by the niobium-doped titanium dioxide. Future work under the subcontract will be directed at increasing the efficiency of the cells by decreasing this absorption in the titanium dioxide, and by forming microcrystalline, instead of amorphous, p-type silicon layers.

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Revised Task Statement

In view of discussions at the Guidance Team Meeting in May, 1995, and with team members and NREL staff, we have revised the Task Statement for the current phase of the contract to read as follows:

Task 1. Optimize the ratio of the electrical conductivity to the visible absorption for fluorine-doped zinc oxide (ZnO:F) films made by a more robust APCVD process from less hazardous precursors. The goal will be to deposit ZnO:F films over an area of 10 cm by 10 cm with a sheet resistance of less than 12 ohms per square, thickness uniformity + 5%, visible haze of about 10 to 15%, and optical absorption of less than 4% at 550 nm.

Task 2. Deposit electrically conductive, transparent tin oxide and/or titanium oxide films on textured silver back electrodes, and then deposit amorphous silicon solar cells on these electrodes. Vary the thickness of the tin oxide and titanium oxide in order to optimize the efficiency of the solar cells.

Task 3. Prepare transparent conductors having the structure glass/textured ZnO:F/smooth TiO₂:Nb. Use these structures as substrates for the deposition of amorphous silicon cells having microcrystalline p-layers.

About one-third of the current project resources are allocated to each of these three objectives.

A superstrate amorphous silicon solar cell incorporating these new materials could have the following structure:

glass
ZnO:F
TiO ₂ :Nb
uc-Si:B
a-Si
uc-Si:P
ZnO
Al or Ag

A substrate amorphous silicon solar cell incorporating these new materials could have the following structure:

ZnO
uc-Si:B
a-Si
uc-Si:P
TiO ₂ :Nb
SnO ₂ :F or ZnO:F
Al or Ag
Stainless Steel

Task 1. Optimize the Ratio of the Electrical Conductivity to the Visible Absorption for Fluorine-doped Zinc Oxide Films Made by a More Robust APCVD Process from Less Hazardous Precursors

Why use ZnO:F? It has the lowest absorption loss of any known transparent conductor. ZnO:F was discovered under a previous NREL contract, and its superior properties documented.

New samples were prepared with several thicknesses of textured ZnO:F in order to find the thickness which provides the most efficient cells. Samples were sent to the NREL team members Steven Hegedus at the University of Delaware, who fabricated amorphous silicon solar cells on

these samples. The cells showed the expected currents, but the voltages and fill factors were lower than those made on control samples of tin oxide. Probably these problems arise from high contact resistance at the interface between the zinc oxide and the p-type amorphous silicon. Further collaborative work will be carried out in order to solve this contacting problem.

In discussions with NREL technical personnel and guidance team members, we decided to redirect some of the efforts under this task toward the problem of improving the reproducibility of ZnO:F production, and its use in amorphous silicon solar cells. In particular, pilot production at Solarex had problems reproducing the quality (conductivity and haze level) of ZnO:F produced by their Watkins-Johnson belt furnace. Although some samples had outstanding properties, lack of consistent quality hampered optimization of the use of this material.

Our analysis of this problem is that diethylzinc, the very reactive zinc source used in the deposition reaction, is very sensitive to oxygen and water vapor. Both O_2 and H_2O are expected to be common contaminants in the atmosphere inside the belt furnace, which ideally should be pure nitrogen. Therefore, a more robust manufacturing process must be based on reactants which are less sensitive to oxygen and water.

One less reactive zinc source is zinc acetylacetonate. It does not react with oxygen or water at room temperature, although it does readily adsorb water of hydration from a moist atmosphere. Thus we began a study of its use as a source for the more reproducible CVD of ZnO:F. Commercially available zinc acetylacetonate is only partially volatile because it contains water of hydration. We removed the water of hydration by recrystallization from methanol solution, followed by heating to remove the methanol of crystallization. The resulting anhydrous material can be evaporated from a bubbler containing its melt at about 130 °C.

CVD reactions of zinc acetylacetonate were carried out in an atmospheric pressure reactor using soda-lime glass substrates 10 cm wide placed on an electrically heated nickel plate. A second nickel plate was held with its bottom surface 0.6 cm above the top of the glass plate. The reactant gas mixture was distributed through a 10 cm long row of small holes near one side of the glass substrate. The gas mixture then flowed through the 0.6 cm by 10 cm channel between the glass plate and the upper nickel plate, and out into the atmosphere in an enclosed hood. Any zinc acetylacetonate vapor that had not reacted inside the CVD chamber then reacted with

water vapor in the atmosphere and deposited as a powder on the exterior surface of the apparatus. Nitrogen carrier gas flow rates of about 10 liters/minute were used.

Zinc acetylacetonate vapor was found to deposit films on glass substrates heated to temperatures around 500 °C. However, these films were not pure zinc oxide, for they showed strong absorption of visible light. The absorption could be removed by adding either water vapor or oxygen to the reaction. Water vapor was fed into a separate row of holes from the zinc acetylacetonate vapor, in order to avoid premature reaction between these reactants. Water vapor was found to react with zinc acetylacetonate vapor at substrate temperatures of about 400 to 450 °C to deposit highly transparent films of pure zinc oxide. Oxygen was found to react with zinc acetylacetonate vapor at substrate temperatures of about 500 to 600 °C to deposit highly transparent films of pure zinc oxide. A minimum oxygen concentration of about 15 mole % oxygen was needed to remove the visible absorption from films deposited at about 550 °C. Unlike the water vapor, the oxygen gas could be premixed with the zinc acetylacetonate vapor without premature reaction.

These zinc oxide films have low electrical conductivity, near $10 \Omega^{-1}\text{cm}^{-1}$, and thus are not suitable as electrodes for solar cells. Fluorine is the ideal dopant for increasing the electrical conductivity of zinc oxide films. Therefore a suitable fluorine-containing material was sought in order to introduce fluorine into the CVD zinc oxide. Hexafluoropropene gas was investigated first as a potential fluorine source, because this dopant gas was successfully used in our previous work with diethylzinc. Introduction of hexafluoropropene gas into the CVD reaction of zinc acetylacetonate and water vapor did not show any evidence of increased conductivity of the zinc oxide, and no fluorine was detected in the film.

Hydrogen fluoride was tried as a dopant, along with water vapor as an oxygen source. The HF and water vapor were fed into a separate row of holes from the zinc acetylacetonate vapor, in order to avoid any premature reaction between the reactants. HF did increase the conductivity to $100 \Omega^{-1}\text{cm}^{-1}$, and fluorine contents up to 0.6 atomic per cent were observed in the film. The results are presented in Table 1, which gives the substrate temperature during deposition (T_s), the electrical conductivity of the film (σ), the mobility (μ) and concentration (n) of the conduction electrons, the fluorine concentration ($[F]$), and the doping efficiency, defined as 100%

times the ratio of the conduction electron concentration to the fluorine concentration, $(n/[F]) \times 100\%$.

Table 1. Electrical Properties of Fluorine-Doped Zinc Oxide Films Prepared from Zinc Acetylacetonate, Water Vapor and Hydrogen Fluoride.

T_s °C	σ $\Omega^{-1}\text{cm}^{-1}$	μ $\text{cm}^2/\text{V}\cdot\text{sec}$	n cm^{-3}	[F] atomic %	doping efficiency(%)
300	90	14	3.8×10^{19}	0.6	5.5
350	100	20	3.1×10^{19}	0.3	11.4
400	42	28	0.9×10^{19}	0.2	5.3
500	32	21	1.0×10^{19}	0.2	5.5
550	40	7	3.7×10^{19}	<0.1	>41

Although this reaction was successful in producing fluorine-doped zinc oxide, most of the fluorine is electrically inactive. Thus the free electron concentrations and electrical conductivities are an order of magnitude lower than those achieved by our earlier CVD system using diethylzinc.

More conductive fluorine-doped zinc oxide films were obtained by using oxygen, rather than water vapor, as the oxygen source. CVD from zinc acetylacetonate, oxygen and hexafluoropropene produced some films with conductivities as high as $1000 \Omega^{-1}\text{cm}^{-1}$. Experiments varying the hexafluoropropene gas concentration showed that the conductivity decreased for concentrations below about one per cent. For concentrations above about five per cent, and for substrate temperatures above about 550 °C, some etching of the glass substrate occurred, and the CVD process was disrupted in those areas. Therefore we coated the glass surface with a layers that should resist etching by fluorine-containing gases. Because aluminum oxide and titanium oxide are materials that resist etching by aqueous hydrogen fluoride, we tried precoating the substrate with films of alumina or titania. Such precoating of the glass should also prevent sodium from diffusing out of the glass into the zinc oxide coating. Aluminum oxide

coatings were applied by spray pyrolysis from aluminum diisopropoxide ethylacetoacetate, and titanium dioxide coatings were made by CVD from titanium isopropoxide.

The conductivity tended to be lower in the region where the reactant gases flow into the reactor, and higher in the region near the exhaust port. This observation suggests that the fluorine dopant is being converted by chemical reactions within the CVD reactor into a more active fluorine dopant. In order to understand this conversion process better, several experiments were done. First, a separate gas stream of hexafluoropropene and nitrogen carrier gas was preheated to temperatures above the deposition temperature, and then mixed into the other gases just prior to entering the CVD reactor. No change in doping behavior was noted. This experiment rules out purely thermal decomposition as activating the precursor. Next, oxygen was mixed into the hexafluoropropene and preheated. This had a marked effect of increasing the effectiveness of the dopant, but also increased the etching of the glass surface. Thus reaction of the hexafluoropropene with oxygen plays an important role in activating the fluorine dopant.

Preheated mixtures of oxygen and hexafluoropropene were passed over coatings of aluminum oxide and of titanium oxide on glass at 550 °C. The titanium oxide coatings were etched by this treatment, but the aluminum oxide films were unchanged. Deposition of fluorine-doped zinc oxide from zinc acetylacetonate, oxygen and hexafluoropropene was carried out on aluminum oxide coated glass at 550 °C. No sign of etching was observed on these samples. Therefore we have adopted aluminum oxide coatings as a standard protection of glass surfaces prior to coating with fluorine-doped zinc oxide.

The spray process we used to deposit the aluminum oxide is not well suited to producing larger areas of uniform thickness. The hand-held spray nozzle produces a spot of coating only a couple of centimeters in diameter. Moving the nozzle permits the slow coating of larger areas, but it is impossible to distribute the coating uniformly. Thus we have set up a CVD system which should be capable of coating aluminum oxide uniformly on areas up to 10 cm by 10 cm. As a first attempt, we used a bubbler containing the same compound, aluminum diisopropoxide ethylacetoacetate, which we had used successfully in the spray system. However, no aluminum oxide films were obtained on the substrates. Further tests showed that the aluminum compound had decomposed in the bubbler. Trials at various bubbler temperatures, from 100 to 250 °C, showed that the vapors emerging from the bubbler were organic

compounds formed by decomposition of the aluminum diisopropoxide ethylacetoacetate. No aluminum-containing compounds were found in the vapors. The successful vaporization in the spray process must depend on the very rapid heating of the spray droplets as they approach the hot glass surface.

Thus, in order to provide aluminum-containing vapors for a CVD process, we tried to spray the aluminum diisopropoxide ethylacetoacetate solution into a hot carrier gas stream. Unfortunately, this approach has not proven to be successful either, because material deposited in the plumbing before reaching the CVD chamber. We conclude that a more thermally stable and/or more volatile aluminum source is needed for the CVD process. Therefore several new aluminum compounds have been synthesized, and are being tested as CVD precursors to aluminum oxide films.

When a suitable precursor for large area alumina films has been identified, then the scaling up of the zinc oxide APCVD deposition process should be possible.

Task 2. Deposit Electrically Conductive, Transparent Tin Oxide and/or Titanium Oxide Films on Textured Silver Back Electrodes, and then Deposit Amorphous Silicon Solar Cells on these Electrodes. Vary the Thickness of the Tin Oxide and/or Titanium Oxide in Order to Optimize the Efficiency of the Solar Cells.

A diffusion barrier is needed between the amorphous silicon and the back metal (aluminum or silver) electrode, for the following reasons:

- 1) The barrier should prevent the diffusion of the metal into the amorphous silicon and the consequent degradation of its electronic properties by the introduction of traps, scattering centers and recombination centers.
- 2) The barrier should enhance the reflectivity to red light of the metal/silicon interface. To function effectively in this role, the barrier

should have a small real part to its refractive index, and a negligible imaginary part, at optical frequencies corresponding to red light.

3) The barrier material should have low contact resistances to silicon and to the metal (which requires a suitable work function and a sufficiently high free electron concentration).

4) The barrier material should produce a low recombination velocity at its interface with silicon (which requires a low concentration of recombination centers at the interface).

5) The barrier material must be chemically and mechanically stable, and, in particular, must not react with silicon or the reflective metal.

The most commonly used back diffusion barrier is zinc oxide. However, optical measurements have shown that the silver-zinc oxide interface does not reflect as much light as theory, based on the bulk optical properties of these materials, predicted. The physical origin of this discrepancy is not known.

One possible mechanism is diffusion of silver into the zinc oxide, increasing its optical absorption. We have observed an analogous behavior of silver diffusing into zinc sulfide films at room temperature, leading to a darkening of the film. Zinc oxide crystals have an open, tetrahedral network structure that leaves sufficient open space to permit rapid diffusion of silver through the zinc oxide lattice.

Another possible mechanism is surface oxidation of the silver by reaction with the adjacent oxide. Silver oxide is a very dark material which strongly absorbs visible light, so that even a very thin layer of silver oxide could reduce the reflectivity. Silver oxide is not very stable thermodynamically, so its formation by direct reaction with zinc oxide is improbable. However, during deposition of the layers by sputtering or evaporation, they may be exposed to ion bombardment or high temperatures, which may promote the formation of an interfacial silver oxide layer.

Experiments are planned to try to distinguish these or other mechanisms which can reduce the amount of light reflected from the back surfaces of cells.

Possible improved back diffusion barrier material

In order to prevent the interaction of silver with the rest of the cell, it may be desirable to replace the zinc oxide with a material which is more resistant to diffusion or reaction, and at the same time is transparent and electrically conductive. Either titanium oxide or tin oxide should be much better diffusion barriers than is zinc oxide, because the structure of these oxides is a nearly close-packed arrangement of oxide ions that does not have the open space available for diffusion in zinc oxide.

One reason that zinc oxide has been preferred to tin oxide for back contacts on superstrate cells, is that zinc oxide can be deposited in electrically conductive form at the low temperatures (below 250 °C) required for superstrate cells. Tin oxide and titanium oxide are more difficult to deposit in an electrically conductive form at temperatures below 250 °C.

However, for substrate cells grown on metal back contacts, higher deposition temperatures may be used to deposit electrically conductive diffusion barriers for back contacts, because the thermally sensitive amorphous silicon is deposited later. Thus we deposited titanium oxide and tin oxide on silver back contacts, and tested their optical reflection, to see how it compares to the reflection from silver coated with zinc oxide.

Textured silver-coated stainless steel was provided by Dr. Subhendu Guha at United Solar Systems. We first tested the thermal stability of these substrates, before coating them. The total reflection of the silver substrates, including both specular and diffuse components, rises from around 90% at the blue end of the spectrum, to nearly 98% in the red (see the Ag only curve in Figure A). Heating a sample to 500 °C in a nitrogen atmosphere for 30 minutes reduced the reflectivity considerably, to around 70%. This degradation may be due to oxidation by oxygen or water vapor impurities in the nitrogen atmosphere. In a second experiment, another sample was annealed for 7 minutes under the same conditions; its reflectivity was reduced by just a few per cent.

Based on these annealing experiments, CVD of titanium dioxide was carried out with as little preheating of the silver as possible (about 2 minutes before deposition). The deposition of undoped titanium dioxide was carried out using titanium isopropoxide vapor in nitrogen carrier gas at 500 °C in an atmospheric pressure CVD system. The samples were moved through the deposition region on a platform in order to achieve better uniformity of thickness. The niobium-doped titanium dioxide samples

used either 2.5 mole % or 5 mole % niobium ethoxide (mole percentages relative to the titanium isopropoxide) and 5 mole % cyclohexenone, which increases the conductivity.

Previous analyses (by Rutherford Backscattering Spectroscopy) of films prepared under these conditions showed that the percentage of niobium incorporated into these films closely approximates the mole ratios in the vapor. Witness glass plates were placed under or next to the metal substrates during deposition, so that thicknesses could be measured by ellipsometry, which is not possible on the rough silver substrates. Ellipsometer measurements of the titanium oxide films on glass showed that they are approximately 0.05 micron thick, with refractive index between 2.34 and 2.39.

Reflectivities for these TiO_2 /silver/stainless steel samples, shown in Figure A, oscillate from just below 80% to just over 90%, because of interference effects between reflections from the two interfaces of the TiO_2 . Addition of niobium dopant decreases the reflectivity in the blue end of the spectrum, but increases it in the red. The decrease in the blue may be explained by additional absorption in the film, while the increase in the red may just result from differences in the thickness of the different samples shifting the interference pattern.

Solar Cells on ZnO/TiO_2 /silver/stainless steel

United Solar Systems deposited samples of their standard zinc oxide on the TiO_2 /silver/stainless steel just described. The ZnO was grown during one deposition run using a large area DC magnetron sputtering machine. The ZnO thickness is about one micron. Figure B shows the optical reflectivity of the resulting ZnO/TiO_2 /silver/stainless steel back contacts. The curve in Figure B marked 'Ag only' actually has both the ZnO and the silver, but no titanium oxide. The curve for TiO_2 :5%Nb oscillates about the curve with no TiO_2 . The curves for lower or no niobium show **lower** reflectivity than for 5% Nb. Thus increasing the niobium content increases the reflectivity, which is just the opposite trend shown in Figure A for the reflectivity of TiO_2 /silver/stainless steel. The reflectivity trend for the ZnO -overcoated samples might be explained by the niobium dopant lowering the refractive index of the titanium dioxide.

United Solar System next deposited their standard a-SiGe:H solar cells on the ZnO/TiO_2 /silver/stainless steel back contacts in consecutive runs using identical deposition parameters. The solar cells were made in the NIP

configuration. (i.e. N-layer grown first, light shines through the P-layer). The intrinsic material has a Tauc gap of about 1.45 eV; the i-layer thickness is about 0.25 micron. Each sample is then coated with many separate ITO front electrodes having areas of 0.05 or 0.25 cm².

Figure C shows the spectral response (Q) of the 0.05 cm² solar cells, measured at short circuit. In general, the presence of the TiO₂ had very little effect on the spectral response curves. Table 1 gives some properties measured for these cells.

Sample Description	Jsc ma/cm ²	FF	Voc volts	Rs Ω-cm ²	Jsc>630 nm ma/cm ²
no TiO ₂	20.5	0.53	0.746	10.5	8.82
TiO ₂ undoped	20.7	0.51	0.738	11.9	8.71
TiO ₂ with 5% niobium	20.1	0.51	0.731	11.8	8.30

Table 2. Electrical Properties of solar cells having the structure ITO/ μ c-Si:B/a-Si-Ge/a-Si:P/ZnO/TiO₂/Ag/SS, with and without TiO₂.

The current and voltage are hardly changed by the addition of an undoped TiO₂ layer. It is difficult to judge whether the small differences in fill factor and series resistance are significant. Addition of a 5% niobium-doped TiO₂ layer results in a slight reduction (0.4 ma/cm² or 2%) in the current, mainly in the red end of the spectrum. Measurements were also made on Voc in room-light, which is sensitive to shunting. No statistically significant reduction of shunting was produced by addition of the TiO₂ layer.

These results demonstrate that a TiO₂ layer may be added to the substrate cell structure with little change in properties. Doping by niobium is not necessary to achieve satisfactory electrical properties for the cell. Future investigations should include the effect of TiO₂ thickness on solar cell performance.

much higher front surface reflectivity than conventional cells made on textured tin oxide substrates. Meaningful electrical measurements on these samples were not possible, because of high series resistance in the undoped textured zinc oxide back contacts. However, even if low-resistance doped textured back contacts were developed, it is clear that cells with this design would be less efficient than conventional front-surface textured cells, because of their high reflectivity. Thus no further work will be carried out in this subcontract on the proposed Penn State Design.

Task 3. Deposit and Evaluate Niobium-Doped Titanium Oxide as a Transparent Conducting Layer on which More Efficient and More Stable Cells Can Be Deposited.

There are several potential advantages to inserting a transparent, conductive layer of titanium dioxide between the top zinc oxide and the silicon layers of a superstrate solar cell:

- 1) The titanium dioxide is stable enough so that microcrystalline p-silicon could be deposited directly on it. Cells with this structure are expected to have increased voltage and current.
- 2) The titanium dioxide layer would reduce the reflection of light, because it has a refractive index (about 2.3) which is intermediate between that of zinc oxide (1.9) and silicon (about 3). This effect should provide increased current.
- 3) One possible source of instability in amorphous silicon solar cells is the reduction of the transparent metal oxide by the silicon. According to the thermodynamic free energies of these materials, such a reduction reaction with silicon is possibly spontaneous for tin oxide and zinc oxide, but not for titanium oxide, which should thus provide increased stability.

Polycrystalline titanium dioxide films about 0.05 micron thick were deposited on top of fluorine-doped tin oxide films by CVD from titanium isopropoxide at 500 °C. In order to make a quick test of how protective these films were to chemical attack by hydrogen, we treated these films with nascent hydrogen generated by mixing zinc dust and hydrochloric acid. Bare tin oxide films are dissolved within a few seconds by this

treatment. Even after one minute of etching with this mixture, the thin overcoating of titanium dioxide prevented the tin oxide from dissolving. After several minutes of etching, a few spots became etched, presumably by attack through pinholes in the titanium dioxide film. The films did develop a slight gray color during this treatment, which may indicate that some hydrogen diffused through the titanium dioxide film and slightly reduced the tin oxide film.

We thought that perhaps this diffusion takes place by diffusion of the hydrogen through grain boundaries in the titanium dioxide film. A film with amorphous structure would not have such grain boundaries, and thus might be a better barrier to hydrogen diffusion. Therefore we deposited amorphous titanium dioxide films by CVD from titanium diisopropoxide diacetylacetonate. These films also protected the tin oxide from dissolution by zinc and hydrochloric acid, but the darkening of the tin oxide layer also took place on these samples. Thus the amorphous titanium dioxide films were not better diffusion barriers to hydrogen than the polycrystalline titanium dioxide films. Because the electrical conductivity of the polycrystalline films is much higher than that of the amorphous films, future work will concentrate on the polycrystalline titanium dioxide diffusion barriers.

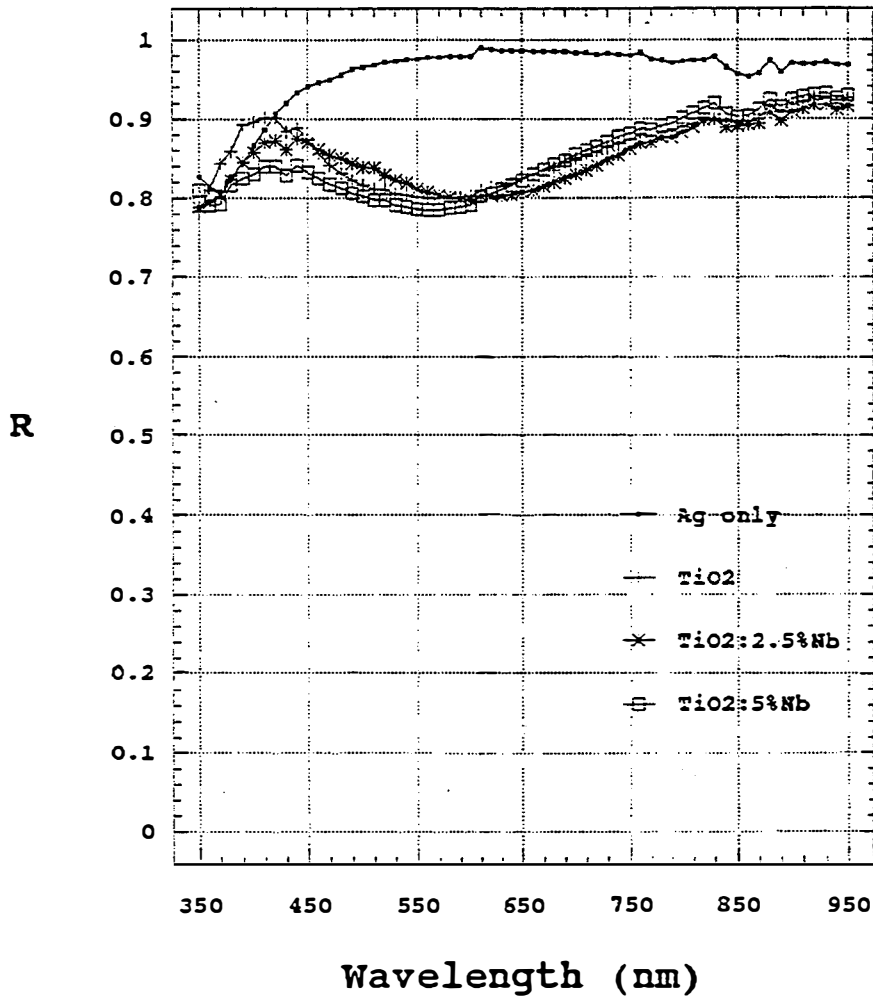
Another approach to reducing the permeability of a polycrystalline diffusion barrier would be to deposit several thinner layers on top of each other. Each new layer would nucleate in new locations on top of the previously deposited layer, thus blocking some of the diffusion pathways along the grain boundaries. In order to test this idea, multilayers of niobium-doped titanium dioxide were deposited on aluminum substrates to a total of about one micron in thickness. Samples were made with one, two, four or eight sublayers of titanium dioxide. All the layers were deposited by APCVD from titanium isopropoxide under the same conditions at 500 °C. The sublayer thicknesses were varied by using different speeds for moving the substrate through the deposition region. In order to test the effectiveness of these layers as diffusion barriers, they were subjected to electrochemical etching in hydrochloric acid solution. All the samples showed a few localized areas of etching after a few minutes. The two-layer samples had the fewest areas of failure, but the differences between the samples were small and may not be significant. The etched areas probably represent pinholes or other defects in the films, rather than diffusion through the films. The deposition of pinhole-free films would need to be carried out in clean-room conditions not available in our laboratory. We can conclude that, aside from localized defects, polycrystalline titanium dioxide films are good barriers against acid attack,

whether they are deposited in one pass or in several successive faster passes through the CVD system.

Diffusion of hydrogen through titanium dioxide bilayers was tested by depositing the bilayers on tin dioxide films. Then the composite samples were reduced by atomic hydrogen, to see if the hydrogen permeates through the titanium dioxide bilayers. The performance of polycrystalline titanium dioxide bilayer diffusion barriers was not significantly different than single layers of the same thickness. Thus the simpler one-pass layers will be used in future tests of titanium dioxide barriers.

A

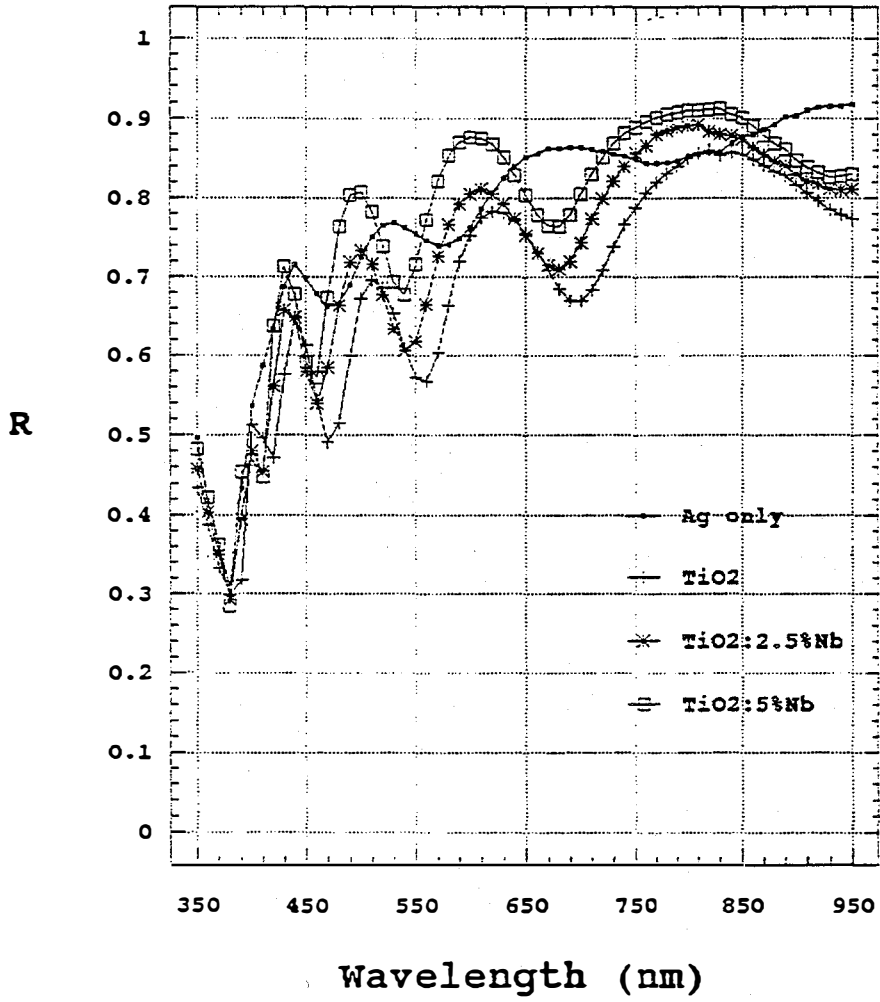
TiO2 Study
Ag / TiO



Harvard TiO2

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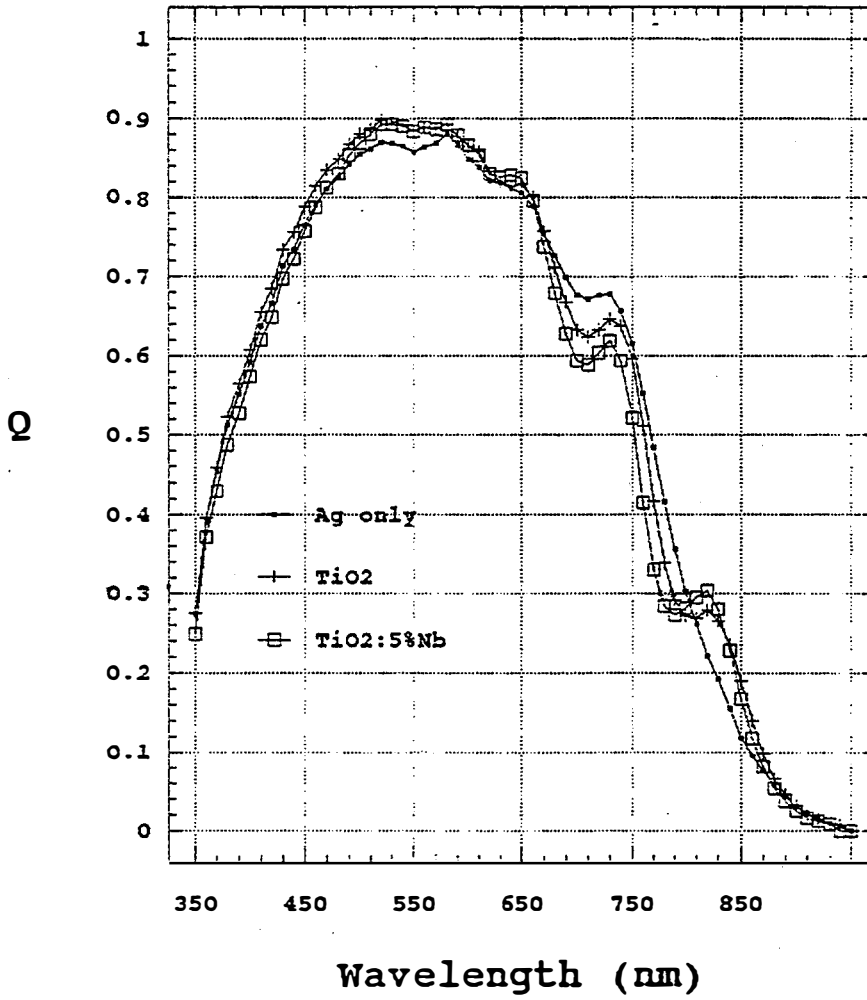
TiO₂ Study
Ag / TiO₂ / ZnO



Harvard TiO₂

C

TiO₂ Study Solar Cells



Harvard TiO₂

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1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE August 1996	3. REPORT TYPE AND DATES COVERED Annual Technical Report, 1 April 1995 - 31 March 1996	
4. TITLE AND SUBTITLE Optimization of Transparent and Reflecting Electrodes for Amorphous Silicon Solar Cells: Annual Technical Report, 1 April 1995 - 31 March 1996		5. FUNDING NUMBERS C: XAN-4-11318-05 TA: PV631101	
6. AUTHOR(S) R.G. Gordon, H. Sato, H. Liang, X. Liu, and J. Thornton		8. PERFORMING ORGANIZATION REPORT NUMBER	
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry Harvard University Cambridge, MA 02138		10. SPONSORING/MONITORING AGENCY REPORT NUMBER TP-451-21583 DE96013074	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393		11. SUPPLEMENTARY NOTES NREL Technical Monitor: B. von Roedern	
12a. DISTRIBUTION/AVAILABILITY STATEMENT		12b. DISTRIBUTION CODE UC-1262	
13. ABSTRACT (<i>Maximum 200 words</i>) The general objective is to develop methods to deposit materials that can be used to make more-efficient solar cells. The work is organized into three general tasks. Under the task to develop improved methods for depositing and using transparent conductors of fluorine-doped zinc oxide in amorphous silicon cells, we demonstrated that fluorine-doped zinc oxide is the most transparent conductor, for a given electrical sheet resistance, of any known material, and we showed how to deposit it by low-cost, high-productivity chemical vapor deposition at atmospheric pressure. Under the task to deposit and evaluate titanium oxide as a reflection-enhancing diffusion barrier between amorphous silicon and an aluminum or silver back-reflector, we found that a titanium dioxide layer could be inserted over the metal back-reflector without loss of optical or electrical characteristics, but a gain in cell stability or efficiency has not yet been demonstrated. Under the task to deposit and evaluate electrically conductive titanium oxide as a transparent conducting layer on which more efficient and more stable superstrate cells can be deposited, thin niobium-doped titanium dioxide films were deposited on top of tin oxide films and were found to protect the tin oxide against chemical etchants. These bilayer films were also used as substrates for growing amorphous silicon solar cells. These cells had normal voltages and fill factors, but lower currents because of some optical absorption by the niobium-doped titanium dioxide.			
14. SUBJECT TERMS photovoltaics ; amorphous silicon solar cells ; fluorine-doped zinc oxide ; back reflectors ; titanium dioxide diffusion barriers		15. NUMBER OF PAGES 27	16. PRICE CODE
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL