Optimization of Transparent and Reflecting Electrodes for Amorphous Silicon Solar Cells

Annual Subcontract Report 1 April 1994 – 31 March 1995

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1617 Cole Boulevard
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ABSTRACT

Transparent and reflecting electrodes are important parts of the structure of amorphous silicon solar cells. We report improved methods for depositing zinc oxide, deposition of tin nitride as a potential reflection-enhancing diffusion barrier between the a-Si and back metal reflector, and evaluation of titanium oxide to protect the electrodes. Highly conductive and transparent fluorine-doped zinc oxide was successfully produced on small areas by atmospheric pressure CVD from a less hazardous zinc precursor, zinc acetylacetonate. The optical properties measured for tin nitride showed that the back-reflection would be decreased if tin nitride were used instead of zinc oxide as a barrier layer over silver or aluminum. Niobium-doped titanium dioxide was produced with high enough electrical conductivity so that normal voltages and fill factors were obtained for a-Si cells made on it. Future work will concentrate on increasing the transparency of the $\text{TiO}_2\text{:Nb}$ and depositing microcrystalline Si p-layers on it, so that the cell efficiencies may be increased.

Preface

This report presents results obtained during the first 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 Hirotoshi Sato was responsible for deposition of fluorine-doped zinc oxide films and measurements of their properties. Post-doctoral fellow Jianhua Hu deposited and characterized the tin nitride films. Graduate student Haifan Liang prepared the doped titanium dioxide films and measured their properties. Undergraduate student Sandrita Benedeck prepared some fluorinated titanium precursors. 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.

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 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 tin nitride 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 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- μ c Si
i-aSi
n-aSi
Sn ₃ N ₄ or 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 best transparent conductor, since it has the highest transparency, 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.

During this phase of the NREL contract, we identified a non-hazardous zinc precursor, and showed that it could be used in a reproducible APCVD process to produce highly transparent, electrically conductive ZnO:F films over small areas of glass. Research during the next phase of the NREL contract will be directed toward scaling up this process to coating 10 cm by 10 cm glass substrates.

Tin Nitride

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 tin nitride as a possible replacement for zinc oxide. Tin nitride has a more densely packed crystal structure than zinc oxide, and thus it may be a better diffusion barrier than zinc oxide. Unfortunately, the optical properties of tin nitride turned out to be less favorable for this application than zinc oxide. During the next phase of the contract, we will investigate alternative materials for transparent, electrically conductive diffusion barriers.

Titanium Dioxide

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). Titanium dioxide is a more stable oxide, and research under this phase of the contract was directed toward making this normally insulating oxide into an electrical conductor. Three different dopants, niobium, tantalum and fluorine, were tested, and niobium was found to give the most conductive material.

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

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.

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Task 1. Develop Improved Methods for Depositing and Using Transparent Conductors of Fluorine-Doped Zinc Oxide in Amorphous Silicon Solar Cells

Why use ZnO:F? It has the lowest optical absorption loss of any known transparent conductor. ZnO:F was discovered under our previous NREL contracts (XG-0-19121-1 and XH-1-11032), and its superior properties documented.

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 initial analysis of this problem is that the deposition reaction is very sensitive to oxygen and water vapor, both of which 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 such 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. The resulting anhydrous material can be evaporated from a bubbler containing its melt at about 130 °C.

Zinc acetylacetonate vapor was found to deposit films on substrates heated to temperatures around 500 °C. However, these films were not pure zinc oxide, for they showed strong absorption of visible light. Water vapor was found to react with zinc acetylacetonate vapor at substrate temperatures of about 400 to 450 °C to deposit highly transparent (>90%) films of pure

zinc oxide. Oxygen was also found to react with zinc acetylacetonate vapor at substrate temperatures of about 500 to 600 °C to deposit highly transparent (>90%) films of pure zinc oxide. These zinc oxide films have low electrical conductivity, around $10 \Omega^{-1}\text{cm}^{-1}$, 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.

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, some etching of the glass substrate occurred, and the CVD process was disrupted. 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. Further experiments will be carried out to see if conditions can be found which will deposit highly conductive zinc oxide over the whole deposition zone.

Task 2. Deposit and Evaluate Tin Nitride as a Reflection-Enhancing Diffusion Barrier Between Amorphous Silicon and an Aluminum or Silver Back-Reflector.

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.

Possible improved back diffusion barrier material

Tin nitride, Sn_3N_4 , is a material which we investigated as a possible improvement over zinc oxide as a back diffusion barrier with possibly higher reflectivity. We had discovered a APCVD method for depositing electrically conductive tin nitride films at temperatures of 200 to 300 °C, low enough to be compatible with amorphous silicon superstrates. We prepared samples of CVD tin nitride films and subjected them to detailed chemical, electrical and optical analyses. These results have been written up as a draft manuscript, which is included as Appendix A to this report.

The optical and electrical properties reported there should provide the basis for modelling to see if tin nitride offers the possibility of improved performance relative to the currently used zinc oxide layers. Because the NREL optical model for textured thin-film solar cells is not yet available, we carried out some simple calculations of the reflectivity of a planar interface between tin nitride and silver. The results show that throughout the visible and near infrared spectrum, this interface will reflect less light than an interface between zinc oxide and silver. Similar results were obtained for aluminum, the other popular metal for reflective back contacts.

We conclude that reflection from back contacts would be decreased if tin nitride were used to replace zinc oxide. It is unlikely that this negative conclusion would be reversed if a more complete textured optical model were used instead of the simple planar one.

Task 3. Deposit and Evaluate Tantalum-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 zinc oxide and silicon layers of a 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 source of instability in amorphous silicon solar cells is the possible reduction of the transparent metal oxide by the silicon. Such a reduction is possible for tin oxide and zinc oxide, but not for titanium oxide, which should thus provide increased stability.

Thermodynamic stability of the metal oxide to silicon interfaces:

It is possible for silicon to reduce a metal oxide to free metal by reactions such as the following:

The free metal may then diffuse into the amorphous silicon and degrade its semiconductor properties. The silicon dioxide thus created at the interface may also increase the electrical resistance losses of the solar cell. Both of these effects would lower its efficiency. The calculated free energy changes, (ΔG), shown for each of these possible reactions, are negative for tin oxide and zinc oxide, showing that such reductions can happen spontaneously. On the other hand, the free energy change for titanium dioxide is positive, which shows that free titanium metal cannot be formed spontaneously at the interface. Instead, titanium silicide may form spontaneously by the reaction

Any titanium silicide thus formed is very stable, and does not permit free titanium to diffuse into the silicon. Thus amorphous silicon solar cells with titanium dioxide transparent conductors should be more stable than those formed on tin oxide or zinc oxide. Additional evidence for the extraordinary stability of titanium dioxide, comes from our studies of CVD of amorphous silicon from disilane at 500 °C. When either tin oxide or zinc oxide films were tried as substrates, these deposition conditions completely destroyed the oxide film, whereas titanium dioxide substrates were completely stable to these extreme conditions.

Formation of TiO₂:Ta Films

Atmospheric pressure chemical vapor deposition was used to deposit films from vapors of titanium isopropoxide and tantalum ethoxide, along with 2-cyclohexen-1-one. These reactants were evaporated from heated bubblers, through which nitrogen carrier gas flowed. Because of the high boiling points of the precursors, special valves were used, which could operate at temperatures up to 200 °C. The vapor mixtures were combined in a Watkins-Johnson gas dispersion nozzle 10 cm wide. The substrates were carried on a heated plate in a BTU Engineering furnace. The reaction proceeds rapidly (about 20 Angstroms per second) at substrate temperatures of about 480 °C.

The presence of 2-cyclohexen-1-one as a reactant has two important effects on the CVD process:

1) In the absence of cyclohexenone, CVD using titanium isopropoxide as a reactant produces titanium dioxide films, but their nucleation is not reproducible or uniform over the substrate surface. When the cyclohexenone is added, then the titanium dioxide films nucleate uniformly over the substrate surface.

2) In the absence of cyclohexenone, the tantalum doping is confined to a fairly small region of the substrate surface. When cyclohexenone is added, the doping region extends much more uniformly over almost all of the substrate surface.

We suggest that the mechanism by which 2-cyclohexen-1-one reacts is as follows:

2-cyclohexen-1-one normally exists in equilibrium with small amounts of its less stable isomers, the dihydrophenols. As the vapors of the 2-cyclohexen-1-one heat up in the CVD chamber, more of it should transform to the dihydrophenol form by a hydrogen shift. For example, a 1,3 hydrogen shift leads to 3,4-dihydrophenol:

The dihydrophenol can then undergo ligand exchange with the alkoxide ligands on the titanium alkoxide, to form a titanium dienolate:

This titanium dienolate may then rearrange by a series of rapid (1,5) sigmatropic hydrogen shifts:

This last form of the titanium dienolate may then decompose very rapidly by a beta-hydride elimination, which is made facile by the aromatic stabilization of the benzene byproduct:

The resulting titanium hydroxide-alkoxide may then undergo a facile beta-hydride elimination of an alcohol:

The net effect of all of the above steps is to replace two of the alkoxide ligands by an oxygen derived from the 2-cyclohexen-1-one:

A second 2-cyclohexen-1-one reactant may then react by a similar sequence of reactions to remove the remaining two alkoxide ligands, to produce titanium dioxide:

Similar reactions can bring the tantalum dopant into the deposition process at the same time as the titanium dioxide is deposited.

Properties of TiO₂:Ta Films

Measuring the film thicknesses required several different techniques. For films less than about 0.5 μm thick, ellipsometry gave the film thicknesses, and a refractive index of about 2.3. The correct order thickness to be added to the ellipsometer thickness could be determined easily by visual observation of the interference colors. For thicknesses from about 0.5 to 1 μm , a prism coupler could be used to measure the thickness and refractive index. Stylus profilometry was used for films more than about 1 μm thick, because the surface of these thicker films were generally too rough for the optical methods. To make the stylus measurement, a step needs to be etched in the film. However, no convenient wet etch process is available for titanium dioxide films. Therefore a special test substrate was prepared, on which a thin zinc oxide film was first deposited. Then part of the ZnO film was masked with tape, and the exposed part of the ZnO film was removed by hydrochloric acid etch. The titanium dioxide film was then deposited over the patterned ZnO film. After deposition, long soaking in hydrochloric acid lifted off those regions of the titanium dioxide which lay over the ZnO film, leaving a patterned titanium dioxide film.

The doping level was about 5% tantalum (compared to titanium). Sheet resistances of one hundred ohms per square were found for films about one μm thick, corresponding to an effective "bulk" resistivity of 0.01 ohm-cm. At thicknesses corresponding to the antireflection thickness, the films on glass are clear in transmission and have a specular, silvery reflection.

In order to test how thick a titanium dioxide layer might be needed for protection, films of various thicknesses of undoped titanium oxide were deposited on top of zinc oxide films. A quick test for complete coverage was to dip the glass/ZnO/TiO₂ into hydrochloric acid, which rapidly etches zinc oxide, but does not dissolve titanium oxide. We found that layers of titanium oxide about 70 nanometers thick protected the zinc oxide from dissolution, while thinner titanium oxide layers allowed at least portions of the zinc oxide to dissolve. This thickness also corresponds to the antireflection condition for titanium oxide films. Thus we will use titanium oxide layers about 70 nanometers thick to protect the zinc oxide from hydrogen plasma attack during formation of microcrystalline p-layers.

Problems with the Deposition of TiO₂:Ta Films

The deposition of TiO₂:Ta films were not sufficiently reproducible. Thicknesses and conductivities varied widely on runs with nominally identical conditions. Part of this problem has been traced to variations in

the vapor-phase concentrations of the reactants, particularly the tantalum source, which has a low vapor pressure. Tantalum ethoxide will condense on any parts of the plumbing which are not heated to a sufficiently high temperature. Therefore the tantalum source bubbler was moved closer to the deposition chamber, so that a shorter length of tubing needed to be heated. This improved the reproducibility somewhat.

In order to give even more reproducible vapor delivery, a new vapor source was constructed, which delivers the vapor directly to the inlet to the gas distributor. In this system, the liquid titanium and tantalum sources are mixed together and injected from a syringe pump into an ultrasonic nozzle. The resulting aerosol is evaporated into a preheated nitrogen carrier gas. This system supplies vapor at a much more reproducible concentration, and with a well-determined ratio of tantalum to titanium.

Even with this improved vapor supply system, there were significant variations in film properties from run to run. Even minor variations in vapor concentrations and their ratios have large effects. The problem seems to be a chemical inhibition of the titanium dioxide deposition reaction by the presence of the tantalum dopant. At low tantalum ethoxide concentrations, too little tantalum dopant is incorporated into the film, and the conductivity is too low. At higher tantalum ethoxide concentrations, the titanium deposition rate is reduced, and the tantalum doping level jumps to too large values.

Formation of $\text{TiO}_2\text{:F}$ Films

In order to alleviate these problems with tantalum doping, tests were made of fluorine as a dopant source for niobium. Two different sources of fluorine were tried.

In the first attempt at fluorine doping, some fluorine was incorporated into a titanium precursor molecule, in the form of a fluorinated acetylacetone ligand. This seemed like a promising approach, by analogy to similar barium precursors which deposit barium fluoride by CVD. We prepared a new compound, titanium bis-isopropoxide bis-hexafluoroacetylacetonate by reaction of titanium isopropoxide and hexafluoroacetylactone. The reaction mixture was refluxed overnight, and the byproduct isopropanol was then removed by vacuum distillation, resulting in a yellow oil, which was characterized by NMR and mass spectroscopy. Titanium dioxide films deposited from this precursor by APCVD at 480 °C were, however, not electrically conductive.

A second approach to fluorine doping used tertiary-butyl fluoride as a fluorine dopant. This gas was synthesized by the reaction of isopropanol with concentrated aqueous hydrofluoric acid. Using titanium isopropoxide as a titanium source, APCVD at 480 °C deposited transparent, electrically conductive, fluorine-doped titanium dioxide films. The resistivity was, however, higher (over 0.1 ohm-cm) than that of the tantalum-doped films. Another problem with t-butyl fluoride as a fluorine source is that portions of the glass substrates were often etched, so that uniform coverage of the film could not be obtained.

Formation of TiO₂:Nb Films

In order to alleviate these problems with tantalum and fluorine doping, tests were made of niobium ethoxide as a dopant source for niobium. Niobium ethoxide does not appear to show the inhibitory effect shown by tantalum ethoxide. The doping level of niobium appears to be more stable and reproducible than that of tantalum. The compositions of some TiO₂:Nb films were measured by Rutherford Backscattering Spectroscopy. The ratio of niobium to titanium in the films was found to be nearly identical to the ratio in the precursor mixture. Doping levels of up to 15% niobium (compared to titanium) were used.

The niobium dopant is electrically active and dramatically increases the conductivity of the titanium dioxide, particularly in the presence of cyclohexenone. The lowest resistivities were obtained for doping levels of 5 to 10%. Sheet resistances as low as twenty five ohms per square were found for films about two μm thick, corresponding to an effective "bulk" resistivity of 0.005 ohm-cm. Hall effect measurements yielded a free electron concentration of about $2 \times 10^{21} \text{ cm}^{-3}$ for films doped with 10% niobium. This concentration is remarkably high for any doped semiconductor, and is higher than any reported for tin or zinc oxides. The mobility is, however, only $0.7 \text{ cm}^2/\text{Vs}$, which is lower than typical mobilities for tin or zinc oxide. The resistivity increases steeply for thinner films, which have smaller grains and more electron scattering from grain boundaries.

Optical transmission and reflection spectra were taken over the visible and near-infrared regions of the spectrum. The transmission and reflection were subtracted from one hundred per cent to obtain the percentage of light absorbed as a function of wavelength. Then Beer's law and the measured film thicknesses (about 2 μm) were used to determine the

optical absorption coefficients as a function of wavelength. These results are plotted in Figure 1.

FIGURE 1. Optical absorption coefficient of TiO₂:Nb films

As expected, the optical absorption increases with increasing niobium content. For the highly conductive films (>5% niobium), the absorption is far too large for TiO₂:Nb to form an efficient solar cell. However, a thin layer of TiO₂ could be used to protect a tin or zinc oxide layer during the deposition of μ ocrystalline p-layers on a composite TCO having the structure glass/ZnO/TiO₂.

In order to test how thick a titanium dioxide layer might be needed for such protection, films of various thicknesses of undoped titanium oxide were deposited on top of zinc oxide films. A quick test for complete coverage was to dip the glass/ZnO/TiO₂ into hydrochloric acid, which rapidly etches zinc oxide, but does not dissolve titanium oxide. We found that layers of niobium-doped titanium oxide as thin as 30 nanometers thick protected the zinc oxide from dissolution, while thinner titanium oxide layers allowed at least portions of the zinc oxide to dissolve.

Stability Of Double Layer TCO Films

We investigated the ability of thin TiO_2 films (20 nm) to protect thicker textured SnO_2 films from plasma damage. APCVD $\text{TiO}_2:10\%\text{Nb}$ films were deposited on APCVD SnO_2 from Solarex. The films were heated to 200 °C and exposed to a 100 mW/cm^2 hydrogen plasma for 5 minutes. This treatment increased the absorption (at 550 nm) of a bare tin oxide film by 5%. The tin oxide film that was covered by a layer of $\text{TiO}_2:10\%\text{Nb}$ only increased its absorption by 3%, thus demonstrating some protective effect. However, the TiO_2 layer was initially more absorbing because of the unnecessarily high Nb doping level.

Amorphous Silicon Solar Cells Grown on Superstrates of Glass/ $\text{SnO}_2:\text{F}/\text{TiO}_2:\text{Nb}$

Textured $\text{SnO}_2:\text{F}$ on low- im glass was coated with about 30 nm of $\text{TiO}_2:\text{Nb}$ (10% Nb) by the APCVD process described above. Amorphous (not microcrystalline) silicon solar cells were then deposited on this double layer TCO by Steven Hegedus at the University of Delaware. Comparison cells made in the same a-Si device deposition on conventional bare tin oxide had essentially equivalent open circuit voltages (0.82 V) and fill factors (0.67-0.69), showing that the $\text{TiO}_2:\text{Nb}$ layer is sufficiently conductive. The short-circuit current of the cell with $\text{TiO}_2:\text{Nb}$ was, however, 12% lower than the conventional cell, suggesting the presence of optical absorption in the $\text{TiO}_2:\text{Nb}$ layer in agreement with absorption measured on the $\text{SnO}_2/\text{TiO}_2:\text{Nb}$ layers. In future tests, lower niobium concentrations will be used, along with plasma conditions for micro-crystalline p-layers, in order to achieve cells with increased efficiency.

Appendix A

Electrical and Optical Properties of Tin Nitride Thin Films Prepared by Metalorganic Chemical Vapor Deposition

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Tin nitride thin films have been successfully prepared in an atmospheric pressure chemical vapor deposition reactor from tetrakis(dimethylamido)-tin(IV) and ammonia in the temperature range between 200°C and 475°C. Film thicknesses and refractive indices were determined with an ellipsometer. For thick films, a profilometer was used to measure thickness directly. Forward recoil spectrometry showed that hydrogen concentration in the film decreases with increasing deposition temperature. Rutherford Backscattering spectrometry showed that carbon and oxygen concentrations for films deposited at temperatures above 200°C are below the instrument detection limits. Film resistivity and electron concentration were determined with Van der Pauw's methods. Optical measurements showed that film has strong absorption, especially in the short wavelength region. The band gap of tin nitride film was found to be in the range between 2.7 eV and 3.7 eV. A damped Lorenz oscillator was used to describe the dispersion of dielectric functions in the wavelength range between 0.5 μm and 0.8 μm . The calculated optical spectra agree well with those obtained from experiments.

I. INTRODUCTION

Main group metal nitrides have many unique chemical and physical properties and have applications in the microelectronics industry as diffusion barriers, passivation layers, and dielectric layers¹⁻⁴. The Group 14 nitrides such as silicon and germanium nitrides films have been prepared with different techniques and their properties have been studied thoroughly^{5,6}. However, tin nitride has not been studied as extensively as its lighter congeners. There were two early reports in the literature concerning the synthesis of bulk tin nitride from SnCl_4 and NH_3 by dc discharge^{7,8}. In 1975, Remy and Hentzpergue reported the first preparation of tin nitride thin films by reactive cathodic sputtering in a dc diode system^{9,10}. They demonstrated that those films were amorphous by electron diffraction. The film composition was found to be Sn_3N_4 , containing molecular nitrogen and traces of free tin. In contrast to the insulating silicon and germanium nitride, tin nitride films were conductive and the temperature dependence of its electrical conductivity indicated that tin nitride is a semiconductor. Optical absorption measurements showed that the energy gap is between 3.5 and 3.6 eV. Maya recently reported the preparation of bulk tin nitride from the thermal decomposition of tin amide imide, $\text{Sn}(\text{NH}_2)_2\text{NH}$, which is a polymeric compound¹¹. Maya also prepared thin film tin nitride with a technique similar to that used by Remy and Hentzpergue^{12,13}. He demonstrated the thermal instability of tin nitride, which began to decompose into the elements at a maximum rate at 615°C . Schreiner etc. obtained a stable and well crystallized compound with a Sn/N ratio of 1.2 by magnetron sputtering¹⁴. Tin nitride conductivity was also found to strongly depend on the preparation methods and the reported conductivities differ by as much as 10^5 .

Chemical vapor deposition consists of the transport of volatile reactants, usually with a carrier gas, into a reactor. Gas phase reactions occur near and on the hot substrate surface and one of the reaction products is a solid film. The homoleptic metal dialkylamido complexes are a class of interesting compounds for the deposition of metal nitrides because of the direct metal to nitrogen bond. However, the decomposition of these complexes alone could not give clean metal nitride films^{15,16}. Both organic carbon and metal bonded carbon have been detected. The carbon contamination may result from the amido ligand β -hydrogen activation in the precursors with dialkylamido ligands¹⁶. Guided by

solution phase chemistry of transamination reactions¹⁷, ammonia was used to react with metal dialkylamido complexes to produce pure metal nitride films under very mild conditions. This dual precursor system for the preparation of metal nitride has been widely used to deposit many transition and main group metal nitrides in our lab^{1-4,16,18-19}.

We have demonstrated recently that tin nitride film could be prepared by metalorganic chemical vapor deposition from tetrakis(dimethylamido)-tin(IV) and ammonia and some preliminary results were reported². Tetrakis(dimethylamido)tin(IV) is both air and moisture sensitive, and reacts with ammonia even at temperatures below 100°C. It is therefore impractical to premix tetrakis(dimethylamido)tin(IV) and ammonia before they flow into the reactor. Tetrakis(dimethylamido)tin(IV) is also not very thermally stable and begins to decompose to tin metal at temperatures above 300°C in the absence of ammonia^{2,15}.

In this paper, we report that the use of a chemical vapor deposition system with a specially designed nozzle enables us to coat substrates with tin nitride over large areas. Also discussed is the influence of the ammonia concentration and deposition temperature on the structural, electrical and optical properties of the film.

II. EXPERIMENTAL PROCEDURES

Tetrakis(dimethylamido)tin(IV), the precursor to tin nitride deposition, was prepared by the following reaction:

Lithium dimethylamide was prepared by bubbling dimethylamine gas through 0.5 liters of a 1M solution of n-butyllithium in hexane at 0°C until the precipitated product began to dissolve in the hexane. The excess amine and solvent were then stripped off under vacuum until the product was dry. 25.1 g of fine, white $\text{LiN}(\text{CH}_3)_2$ (98.4%) were recovered.

The lithium dimethylamide thus prepared was suspended in benzene, cooled to 0°C and 26.0 g (0.1 mol) of SnCl_4 (Alfa) were diluted in 50 mL of hexane and added dropwise over 30 minutes to the suspension. The resulting mixture was refluxed for 2.5 hours and allowed to stir overnight. It was then filtered over Cellite and the solvent was removed under vacuum, leaving 18.92 g (64.1 %) of a clear, amber liquid, $\text{Sn}(\text{N}(\text{CH}_3)_2)_4$.

^1H NMR in benzene- d_6 showed a strong, sharp signal ($\delta = 2.81$ ppm, singlet). The product was distilled under reduced pressure (50°C , 0.1 mmHg) to afford 14.0 g (74% recovery) of a clear, very faintly yellow liquid that had a ^1H NMR spectrum identical to that of the crude product.

Deposition of tin nitride was carried out in an atmospheric pressure chemical vapor deposition system which is shown schematically in Fig. 1. The nickel reactor has a special nozzle, designed by the Watkins-Johnson Company, with three separated gas inlet lines, which lead to five parallel gas inlet slots. This design is helpful in moderating the fast reaction of tetrakis(dimethylamido)tin(IV) and ammonia. The central line and outer two lines are used to introduce tetrakis(dimethylamido)tin(IV) and ammonia, respectively. The two intermediate lines are for nitrogen buffer gas which keeps tetrakis(dimethylamido)tin(IV) and ammonia separated for a small distance after being injected into the reactor. The reactor is a rectangular chamber 1 cm high, 12.5 cm wide and 30 cm long operating at one atmospheric pressure. Substrates rest on the bottom of this chamber. The reactor was placed on a hot plate, and the thermocouples for the temperature controller were inserted into holes in the bottom plate of the reactor.

The tin precursor tetrakis(dimethylamido)tin(IV) was transferred to a stainless steel bubbler which was maintained at 75°C throughout the experiments. The bubbler has a by-pass line which is used to purge the tin precursor line. Purified in-house nitrogen was used as the carrier gas and diluent for the tin precursor. Ultrahigh-purity ammonia, passed through a Nanochem gas purifier, was diluted further by nitrogen before flowing into the reactor. The flow rates were controlled through Tylan mass flow controllers. Both silicon (p-type, from Silicon Sense, Inc.) and soda lime glass substrates were first cleaned with a sodium-free detergent (Detergent 8, from Alconox, Inc.) and then rinsed with de ionized water. The substrates were blown dry with filtered air after most of the water had sheeted off. The reactor, loaded with substrates and heated to the desired deposition temperature, was purged for at least two hours to drive out oxygen and water before each deposition. After the deposition, the films were allowed to cool slowly in the reactor under a flow of nitrogen.

A Rudolph Research AutoEL-II ellipsometer was used to determine film thickness and refractive indices at $\lambda = 6328$ Å for those films with thickness less than 1500 Å. Thick films were first covered with a piece of Scotch tape and then etched with zinc powder and 4 M hydrochloric acid solution to form a step. A Tencor Alpha-Step 200 profilometer was then used to measure film thickness directly. The electron density and

mobility were obtained from the measured Hall coefficient by using Van der Pauw's method, which was also used to obtain film resistivity²¹. The specular transmittance and reflectance was measured in the wavelength range between 300 nm and 2300 nm on a Hitachi U-4001 spectrophotometer equipped with a 12° specular reflectance attachment and an integrating sphere detector. The absorption within the film was then found by subtraction of the reflectance and transmittance from 100%.

X-ray diffraction measurements were made on a Philips powder crystallography instrument with copper K α radiation. A JEOL JSM-6400 scanning electron microscope (SEM) was used to obtain the crystallite size information.

Rutherford Backscattering and forward recoil spectra (RBS and FRS) of films deposited on silicon substrates were obtained on a General Ionics Model 4117 spectrometer. The Helium ion (He⁺) beam energy was 2.0 MeV. For the FRS experiments, the angle of the incident beam relative to the sample surface was 15°. In this configuration, the detector and the incident beam were at an angle of 150°. The standard for hydrogen concentration calibration was a piece of *a*-Ge:H with a known hydrogen concentration of 3.4 at.%. Data analyses were carried out with the program Spectrum Analysis, written by Patrick M. Smith, Division of Applied Sciences, Harvard University.

III. RESULTS AND DISCUSSION

A. Film deposition

Tin nitride films were deposited on soda lime glass and silicon substrates in the temperature range 100°C to 475°C from tetrakis(dimethylamido)tin(IV) and ammonia. The tin precursor bubbler was maintained at 75 °C and the delivery lines to the inlet and outlet of the bubbler were held at 120 °C. The higher temperature of the delivery lines prevents tetrakis(dimethylamido)tin(IV) from condensing inside the tubing. The carrier gas flow rate for tetrakis(dimethylamido)tin(IV) was kept at 0.23 l/min. The ammonia flow rate were varied between 0.0 and 0.28 l/min to study its influence on film growth rate and film properties. The ammonia dilution and buffer nitrogen flow rates were kept at 1.91 l/min.

Figure 2 shows the growth rate profile as a function of deposition temperature. Film growth rate is not uniform along the gas flow direction.

There is a peak growth rate at each temperature. In a flow reactor operated at atmospheric pressure, deposition was controlled by the gas-phase reactions which change the gas-phase composition along the gas flow direction. The deposition rate is maximized when the flux of film precursors onto the substrate is maximized. When the reactants enter the reactor, they start to mix and react to form film precursors and therefore the film growth rate is low. As the reactant gas mixture moves downstream, there is a net buildup of film precursors in the gas phase that diffuse to the substrate to form film, and so the film exhibits a rising growth rate. The decline of the growth rate after the peak position corresponds to the depletion of the film precursors in the gas phase.

The growth rate of tin nitride at 100°C is much higher than that at other temperatures. As temperatures increased above 200°C, the growth rate decreased rapidly. The peak growth rate was in the range between 2.2 Å/sec and 4.4 Å/sec.

The thermal decomposition of tetrakis(dimethylamido)tin(IV) alone did not deposit tin nitride film. In a control experiment, only a thin layer of black powder was observed on glass substrate at 300°C in the absence of ammonia. When the deposition temperature was above 400°C, there was some grayish powder on the substrate which became metallic and shiny after being rubbed with a piece of paper. Those shiny films have sheet resistances below 1 ohm/square and are highly conductive, and are therefore thought to be tin metal. However, the tin metal films do not adhere strongly to the substrate and can be easily wiped off. No attempt has been made to characterize their properties.

Figure 3 gives growth rate dependence on ammonia flow rate at 300°C. The growth rates are higher at lower ammonia concentrations. However, film peak growth rates become less dependent on ammonia flow when it is above 0.075 l/min. An ammonia flow rate of 0.15 l/min has been used in all other experiments.

B. Film structure

X-ray-diffraction measurements will give useful information about film crystal structure. Figure 4 shows the x-ray diffraction spectra of a film deposited at 475°C on soda lime glass substrate. The ammonia flow rate was 0.15 l/min. This film has a thickness of 0.34 μm, as determined with a profilometer. The higher counts of the spectra in the low angle region are due to the glass substrate. The x-ray diffraction spectra of films deposited at other temperatures are similar to the one deposited at 475°C, and did not have any diffraction peaks. Therefore, x-ray diffraction

measurement indicates that tin nitride films are either amorphous or crystalline with very small crystallite size.

Scanning electron microscopy of a sample deposited at 475°C showed crystallites with size around 0.1 μm . Crystallites sized around 0.1 μm should give x-ray diffraction peaks. The inability of the film to give x-ray diffraction peaks may indicate that the crystallites either have a much smaller size in the direction perpendicular to the substrate plane or those small crystallites are just some conglomerates of amorphous materials. Transmission Electron Microscopy (TEM) detected tiny crystallites (about 10 nm diameter) in films deposited at temperatures of 300 and 400 °C, whereas films deposited at 200 °C were amorphous².

C. Film composition

Rutherford Backscattering and forward recoil spectra were obtained for films deposited on silicon. Figure 5. shows the FRS spectra of tin nitride films deposited at different temperatures on silicon substrates. For comparison, the FRS spectra of a piece of uncoated silicon substrate is also included in the figure. The hydrogen concentration decreases as the deposition temperature increases. The estimated hydrogen concentrations are given in Table I. The film deposited at 100°C has a hydrogen concentration of almost 20 at.%. As the deposition temperature increased to 475°C, the hydrogen concentration decreased to 2.9 at.%.

Figure 6 shows the RBS spectra of two samples deposited at 100°C and 475°C. The film deposited at 100°C has a strong oxygen peak, but very little carbon or nitrogen. The tin nitride samples deposited at temperatures above 200°C can be etched easily with zinc powder and 4M hydrochloric acid. However, the sample deposited at 100°C is not etched under these conditions, perhaps because it contains more carbon or hydrogen impurities. It may be porous because it could easily be oxidized when exposed to air. However, the film deposited at 475°C showed no oxygen or carbon peaks. For films deposited on silicon substrates at temperatures above 200°C, their RBS spectra are similar to the one deposited at 475°C. Carbon and oxygen concentrations in these high temperature films are below RBS detection limits, which are usually 2-3 at.%. Because of the noise on the silicon background and the weak nitrogen signal, no attempt has been made to determine film composition from RBS spectra.

D. Electrical properties

Tin nitride is thought to be a semiconductor due to the temperature dependence of its conductivity. Its bandgap was measured with different techniques and was reported to be in the range between 1.85 and 3.6 eV^{10,13}. Table I also shows the electron concentrations for films deposited at different temperatures on glass substrates. The samples were taken from the position of the peak growth rate. The electron concentrations were determined from the measured Hall coefficient by using Van der Pauw's technique. No data is available for films deposited at temperatures below 200°C because the Hall voltage is too small to be measured. The measured electron concentrations in tin nitride are in a range typical of semiconductors, but about an order of magnitude smaller than those in semiconducting fluorine doped tin oxide, which are usually around $5 \times 10^{20} \text{ cm}^{-3}$. At room temperature, only a much lower concentration of free electrons would be thermally excited from the valence band to the conduction band. Other possible sources of free electrons are interstitial tin and nitrogen vacancies in the film¹⁰. These defects in the crystal may produce donor levels just below the conduction band and lead to the formation of free electrons. Oxygen is one impurity in the film. The replacement of nitrogen by oxygen may also dope tin nitride and create free electrons. Hydrogen may also act as an n-type dopant. Any or all of these doping mechanisms may produce the observed electron concentrations.

Film resistivity was also measured with Van der Pauw's technique. The resistivity is inversely proportional to the electron concentration. Film mobility μ was obtained from the measured resistivity ρ and electron concentration N_e through

$$\mu = 1/\rho N_e e, \quad (2)$$

where e is the electron charge. Electrons in a film with higher mobility undergo less scattering. The best electrical properties of tin nitride have been achieved at a deposition temperature of 300°C because these films have the highest conductivity and mobility.

E. Optical properties

The optical properties of a film may depend on the deposition temperature, ammonia flow rate, and the sample position along the gas

flow in the reactor. Figure 7 shows the refractive index distribution along gas flow direction as a function of deposition temperature. The refractive index was measured by an ellipsometer at $\lambda=632$ nm. The refractive index always has a peak position and can be as high as 3.0 for films deposited at temperatures above 400°C. Figure 8 shows film refractive index dependence on ammonia flow rate.

Tin nitride film has high refractive index and therefore high visible reflectance. Figure 9 shows the optical spectra of a tin nitride film deposited on glass substrate at 475°C. The film was deposited from an ammonia flow rate of 0.15 l/min and has a thickness of 730 Å, and has a maximum reflectance of 42.4% at $\lambda = 750$ nm. As the wavelength moves to near infrared, its reflectance decreases monotonically. In the short wavelength region, the film has very high absorption, which results from the semiconductor absorption edge. As the wavelength moves to near infrared, the absorption decreases rapidly and stabilizes around 10%. Free electrons in the film should not give such a high near infrared absorption, and the abnormally high absorption may due to impurity levels within the tin nitride band gap. Film absorption depends on the deposition temperature, and increases very rapidly with film thickness. Table I gives the absorption at 632 nm (corresponding to helium-neon laser wavelength) for films deposited at different temperatures. The absorption increases from below 5% at 100°C to almost 60% at 475°C. For a film deposited at 300°C, the absorption increased from 7.3% to 26.9% when film thickness increased from 400 Å to 2290 Å. The high absorption in the short wavelength region also makes the film have a golden color in transmitted light.

The optical absorption coefficient α of a semiconductor near the band edge is closely related to its bandgap. For an indirect bandgap semiconductor and photon energy $h\nu$ greater than the band gap energy E_g of the semiconductor, the following equation is used:²³

$$\alpha h\nu = A(h\nu - E_g)^{1/2}, \quad (3)$$

where A is a constant. By neglecting the multiple reflection in the film and the substrate, the approximate transmittance T for the air/film/glass/air structure is given by:²⁴

$$T = (1 - R_{12})(1 - R_{23})\exp(-\alpha t)T_g/(1 - R_{31}), \quad (4)$$

where t is the film thickness, T_g is the measured bare glass substrate transmittance, R_{12} , R_{23} , R_{31} are the reflectance between air/film, film/glass, and glass/air interface. The reflectance at the interface was calculated from the media refractive index. The refractive indices of glass and air were 1.51 and 1.0 and that of the tin nitride was taken to be 2.5 as an approximation. From the measured film and substrate transmittance T and T_g , the absorption coefficient α was derived. By plotting $(\alpha h\nu)^2$ versus photon energy $h\nu$, the band gap E_g was found from extrapolation. Table I listed the bandgap of tin nitride films deposited at different temperatures. The bandgap decreases with deposition temperature.

F. Optical Modeling

The interaction of electromagnetic radiation with matter is described by the dielectric function $\epsilon(\omega)$ according to

$$\epsilon(\omega) = 1 + \chi^{VE}(\omega) + \chi^{FE}(\omega) + \chi^{PH}(\omega), \quad (5)$$

where $\chi^{VE}(\omega)$, $\chi^{FE}(\omega)$, and $\chi^{PH}(\omega)$ are the susceptibilities of valence electrons (VE), free electrons (FE), and polar optical phonons (PH)²³. The dispersion in a particular spectral region is often dominated by a single mechanism, and the dispersion mechanisms can be studied independently in different spectral regions. We are interested in modeling tin nitride film reflectance and transmittance data in the wavelength range 0.5 μm to 0.8 μm , which is the range that is relevant to tin nitride potential applications in a-Si:H solar cells as back diffusion barriers. Tin nitride films have electron concentrations below 10^{20} cm^{-3} and their optical spectra do not have any phonon dispersion behavior in the wavelength range 0.5 μm to 0.8 μm . The main contribution to the dielectric function in this region is from the valence electrons.

In order to describe the dispersion due to valence electrons, the dielectric function was modeled by a damped Lorentz oscillator²⁵:

$$1 + \chi^{VE}(\omega) = \epsilon_{\infty} + \frac{N_v e^2}{\epsilon_0 m_v^*} \frac{1}{\omega_0^2 - \omega^2 - i\omega\gamma_0}, \quad (6)$$

where ϵ_{∞} is the high-frequency dielectric constant, N_v and m_v^* are the valence electron density and effective mass, ϵ_0 is the permittivity of

vacuum, e is the electron charge, ω_0 describes the excitation frequency of valence electrons, and γ_0 measures the phenomenological damping force. Since ϵ_∞ , N_V , ω_0 and γ_0 are unknown, we write equation (6) in the following form:

$$1 + \chi^{VE}(\omega) = \epsilon_\infty + \frac{p_1}{1 - \left(\frac{p_2}{\lambda}\right)^2 - i\left(\frac{p_2}{\lambda}\right)p_3}, \quad (7)$$

$$p_1 = \frac{N_V e^2}{\epsilon_0 m_V^*}, \quad p_2 = \frac{2\pi c}{\omega_0}, \quad p_3 = \frac{\gamma_0}{\omega_0}, \quad (8)$$

and the parameters ϵ_∞ , p_1 , p_2 and p_3 will be determined by modeling the optical data.

With the dielectric function $\epsilon(\omega) = \epsilon_1(\omega) + i\epsilon_2(\omega)$ constructed above, the complex refractive index $N = n - ik$ can be derived from the given parameters ϵ_∞ , p_1 , p_2 , and p_3 . These parameters will be obtained by modeling the reflectance and transmittance data in the wavelength range 0.5 μm to 0.8 μm . The refractive index n and the extinction coefficient k are related to the dielectric function by

$$n = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} + \epsilon_1}{2}}, \quad (9)$$

$$k = \sqrt{\frac{\sqrt{\epsilon_1^2 + \epsilon_2^2} - \epsilon_1}{2}}. \quad (10)$$

The calculation of reflectance and transmittance is based on the reflection and transmission coefficients at the air/film, film/substrate, substrate/air interfaces. Since the substrate thickness is much larger than the typical wavelength, no interference fringes are observed for bare substrate. The reflectance and transmittance of the bare substrate is therefore found by summation of intensities to take into account the multiple reflection in the substrate. The slight absorption in the substrate is incorporated through an empirical attenuation factor $T_0(\lambda) = \exp[-\alpha_g(\lambda)d]$, which represents the one pass light absorption through the substrate²⁷. $T_0(\lambda)$ and the substrate refractive index $n_g(\lambda)$ are

T and the known air refractive index n_a ($n_a = 1.00029$) through the following equations

$$R = R_g + \frac{T_g^2 T_0^2 R_g}{1 - R_g^2 T_0^2}, \quad (11)$$

$$T = \frac{T_g^2 T_0}{1 - R_g^2 T_0^2}, \quad (12)$$

$$R_g = \left(\frac{n_g - n_a}{n_g + n_a} \right)^2, \quad (13)$$

where R_g is the reflectance between air/substrate interface.

The film thickness is usually below $0.5 \mu\text{m}$ and interference fringes are observed. The reflectance R and transmittance T of a film on a thick substrate are obtained by taking into account the multiple reflection in the film through summation of amplitudes and in the substrate through summation of intensities:

$$R = R_f + \frac{T_f T_b T_0^2 R_g}{1 - R_g R_b T_0^2}, \quad (11)$$

$$T = \frac{(1 - R_g) T_f T_0}{1 - R_g R_b T_0^2}, \quad (12)$$

where R_f and R_b are the bare film reflectance from the air side (front) and from the glass side (back), and T_f and T_b are the corresponding transmittance from the air side and from the glass side. R_f , R_g , T_f , and T_b will be calculated from tin nitride refractive index n and extinction coefficient k and the glass and air refractive index n_g and n_a according to Fresnel's equations²⁶.

With a given set of parameters, the film reflectance and transmittance could be calculated as described above. The more interesting question is to find parameters to fit the optical properties of the films. A minimization program (VG02AD) from the Harwell library is used to minimize the maximum deviation between the experimental and theoretical spectra data. Given some initial estimates of parameters, the program finds parameter values which make the calculated spectra as close to the

measured spectra as possible. Table II shows the parameters obtained from optical data fitting. The error, which measures the maximum difference between the calculated and measured optical data, is below 0.01. The model therefore describes the dispersion mechanism very well in the given wavelength range. The calculated refractive index and extinction coefficients at different wavelengths are given in Table III. Both refractive index and extinction coefficient increase with deposition temperature. By assuming the extinction coefficient to be given by these optical fits, ellipsometry was also used for thickness determination. Table II shows that there are some discrepancies between film thicknesses obtained from ellipsometry measurements and those from optical modeling.

For thicker films with higher absorption, a residual term η has to be added to the equation (7) to account for background absorption, and it is expected that its magnitude depends on the fabrication conditions²³. A calculation was carried out between 0.5 μm and 0.8 μm for a tin nitride film deposited at 200 °C. The residual term η was found to be -0.255. The thickness obtained from the modeling is 0.234 μm . The high frequency dielectric constant is 3.723 and the three damped Lorentz oscillator parameters p_1 , p_2 , p_3 are 1.382, 0.363 μm , and 0.345, respectively. These parameters were used to predict film reflectance and transmittance beyond 0.8 μm . Figure 10 shows that the measured spectra agree well with those obtained from the calculation in the wavelength range 0.4 μm to 1.7 μm . In the wavelength range above 1.7 μm , there are some discrepancies between the calculated and measured spectra, which may result from some other dispersion mechanisms in the tin nitride dielectric function.

IV. CONCLUSIONS

Tin nitride films have been successfully prepared from tetrakis(dimethylamido)tin(IV) and ammonia in the temperature range between 200°C and 475°C. Film growth rates depend on the deposition temperature and ammonia flow rate. The deposited films are either amorphous or polycrystalline with small crystallite size. Hydrogen exists in the film and its concentration decreases with deposition temperature. For films deposited at temperatures above 200°C, oxygen and carbon were not detected by Rutherford Backscattering spectrometry. However, a film deposited at 100°C was mainly tin oxide. Film resistivity and electron

concentration were determined with Van der Pauw's methods. Films deposited at temperatures above 200°C have resistivities below 0.01 Ωcm and electron concentrations almost 10^{20}cm^{-3} . Film absorption depends on wavelength. High absorption was observed in the short wavelength region, which results from the semiconductor absorption edge. The abnormally high absorption in the near infrared may due to impurity levels in the tin nitride band gap. Tin nitride film bandgap depends on the deposition temperature and is in the range between 2.7 and 3.7 eV. A damped Lorenz oscillator describes very well the dispersion in tin nitride dielectric functions in the wavelength range between 0.5 μm and 0.8 μm .

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Table I. The deposition temperature T_d , thickness t , electron concentration N_e , resistivity ρ , mobility μ , absorption A at $\lambda = 632$ nm, and optical bandgap E_g at room temperature for tin nitride films deposited on soda lime glass substrates at different temperatures. The hydrogen concentrations were determined for films deposited on silicon substrates. Those films usually have thicknesses below $1000\text{\AA}$.

T_d ($^{\circ}\text{C}$)	H^a (at.%)	t^b ($\text{\AA}$)	N_e^c (10^{20}cm^{-3})	ρ^d ($10^{-3}\Omega\text{cm}$)	μ (cm^2/Vs)	A^e (%)	E_g (eV)
100	19.0	4560				4.6	3.64
200	7.9	3650		12.2		24.3	3.06
300	4.0	2290	0.72	2.8	31.0	26.9	3.41
400	4.3	4600	0.96	4.3	15.1	57.5	3.01
475	2.4	3400	0.84	7.7	9.7	59.3	2.69

^afrom FRS, on silicon substrates, the estimated error is 0.5 at.%.

^bfrom profilometer measurements.

^cfrom Hall coefficient measurements.

^dobtained by using Van der Pauw's methods.

^eat $\lambda=632$ nm.

Table II. The deposition temperature T_d , thickness t , high frequency dielectric constant ϵ_∞ , Lorenz parameters p_1 , p_2 , p_3 , and the modeling error σ for tin nitride films deposited at different temperatures on glass substrates. The films were deposited with an ammonia flow rate of 0.15 l/min, and taken from the position of the peak growth rate.

T_d (°C)	t^a (Å)	t^b (Å)	ϵ_∞ (at.%)	p_1	p_2 (μm)	p_3	σ^c
100	1100	907	2.955	0.888	0.285	0.035	0.002
200	520	657	1.773	1.514	0.410	0.057	0.006
300	400	624	1.587	1.932	0.402	0.072	0.008
400	810	667	1.912	2.494	0.375	0.167	0.008
475	730	660	0.313	6.195	0.313	0.277	0.005

^afrom ellipsometry measurements.

^bfrom optical modeling in the wavelength 0.5 μm to 0.8 μm.

^cmeasures the maximum difference between calculated and measured optical data.

Table III. Refractive index n and extinction coefficient k at various wavelengths for tin nitride films deposited at different temperatures. The samples are the same as those in Table II.

T_d	$n(632)^a$	$n(500)^b$	$n(630)$	$n(700)$	$n(800)$	$k(500)$	$k(630)$	$k(700)$	$k(800)$
100	2.145	2.066	2.018	2.005	1.993	0.010	0.006	0.005	0.004
200	2.415	2.510	2.094	2.017	1.955	0.126	0.040	0.029	0.021
300	2.447	2.637	2.200	2.113	2.042	0.167	0.057	0.042	0.031
400	3.073	2.692	2.387	2.316	2.354	0.279	0.122	0.093	0.071
475	3.071	3.147	2.886	2.813	2.745	0.425	0.251	0.212	0.167

^afrom ellipsometry measurements at $\lambda=632$ nm.

^bfrom optical data fitting, the numbers in the parenthesis are wavelength in nm.

Figure 1. Schematic diagram of the apparatus used for the deposition of tin nitride.

Figure 2. Growth rate profile as a function of deposition temperature. The flow rate of carrier nitrogen for tetrakis(dimethylamido)tin(IV) is 0.23 l/min and the ammonia flow rate is 0.15 l/min.

Figure 3. Growth rate profile as a function of ammonia flow rate. The deposition temperature was 300°C.

Figure 4. X-ray diffraction spectra of tin nitride film deposited on soda lime glass substrate at 475°C. The film was taken from the peak growth position and the ammonia flow rate is 0.15 l/min.

Figure-5. FRS spectra of tin nitride films deposited at different temperatures on silicon substrate.

Figure 6 (a). RBS spectra of two tin nitride samples deposited at 100° (a) and 475°C (b) on silicon substrates.

Figure 6(b). RBS spectra of two tin nitride samples deposited at 100° (a) and 475°C (b) on silicon substrates.

Figure 7. Refractive index profile as a function of deposition temperature. The films are the same as those in Figure 2. The refractive index was determined at $\lambda=632$ nm.

Figure 8. Refractive index profile as a function of ammonia concentration. The films are the same as those in Figure 3.

Figure 9. Optical spectra of a tin nitride film deposited at 475°C on soda lime glass substrate. The film was taken from the peak growth position and the ammonia flow rate was 0.15 l/min.

Figure 10. Comparison of measured and calculated optical spectra of a tin nitride films deposited on a soda-lime glass substrate at 200°C.

REPORT DOCUMENTATION PAGE

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13. ABSTRACT (Maximum 200 words) Transparent and reflecting electrodes are important parts of the structure of amorphous silicon solar cells. We report improved methods for depositing zinc oxide, deposition of tin nitride as a potential reflection-enhancing diffusion barrier between the a-Si and back metal reflector, and evaluation of titanium oxide to protect the electrodes. Highly conductive and transparent fluorine-doped zinc oxide was successfully produced on small areas by atmospheric pressure CVD from a less hazardous zinc precursor, zinc acetylacetonate. The optical properties measured for tin nitride showed that the back-reflection would be decreased if tin nitride were used instead of zinc oxide as a barrier layer over silver or aluminum. Niobium-doped titanium dioxide was produced with high enough electrical conductivity so that normal voltages and fill factors were obtained for a-Si cells made on it. Future work will concentrate on increasing the transparency of the TiO ₂ :Nb and depositing microcrystalline Si p-layers on it, so that the cell efficiencies may be increased.					
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