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ABSTRACT

Chemical vapor deposition (CVD) of doped silane has been used by others to deposit a polycrystalline silicon film (polysil) on metal or graphite substrates, but dopant migration to grain boundaries during deposition apparently prohibits attaining a uniform or desired dopant concentration. In contrast, we have used neutron transmutation doping to introduce a uniform phosphorus dopant concentration in commercially available undoped CVD polysil at doping concentrations $\geq 2 \times 10^{15}$ cm^{-3}. Radiation damage annealing to 800°C did not indicate dopant migration. Carrier mobility increased with doping concentration and the minority carrier lifetime (MCL) appears to be comparable to that of neutron transmutation doped (NTD) single crystal Si. Application of this technique to photovoltaic solar cell fabrication will be discussed.

INTRODUCTION

It has long been recognized that thermal neutron irradiation can be used to introduce certain impurity atoms in semiconducting materials as a consequence of the transmutation process.[1] For example, normal isotopic Si contains 3.05% of ^{30}Si which transmutes to ^{31}P after thermal neutron absorption, with a half-life of 2.6 hours. The range of the thermal energy neutrons in Si is two meters, so that it is possible to obtain a very uniform distribution of ^{31}P, a standard n-type dopant in Si. In contrast to this, there is no known method of crystal growth that provides a uniform distribution of any chemical impurity dopant in Si. It has been demonstrated that the distribution of P takes the form of striations which both decrease the minority carrier lifetime and degrade the characteristics of a p-n junction.[2] These striations can be greatly reduced

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by the method of neutron transmutation doping, and it has been shown recently that the performance and yield of high power Si rectifiers, thyristors, and of avalanche detectors can be significantly improved when NTD-Si rather than conventionally doped Si is used in these devices.[3] In each case, higher operating voltages are possible because of the extremely uniform P dopant concentration obtained by the neutron doping process.

An improvement in the efficiency of Si photovoltaic devices (solar cells) may also be attainable through the use of NTD-Si, although for different reasons. Solar cells for terrestrial use require a much higher doping level, and being large area devices they require a uniform macroscopic as well as microscopic doping concentration, which NTD-Si provides. The presence of areal and spatial inhomogeneities in Si is considered by a number of leading device theorists to be one of the primary reasons for not attaining solar cell efficiencies (presently ∿ 15%) that are closer to the theoretically predicted (∿ 20%) values. A small increase in efficiency may not be of particular significance under one-sun conditions. However, it is likely that concentration up to 100 suns may be employed in many solar cell applications, and even a small improvement in efficiency will be significant under these conditions. Another intrinsic characteristic of NTD-Si is that it does not contain other impurities, such as may be introduced in standard doping techniques. Very small (trace) amounts of certain heavy metal impurities, e.g. Ag, Au, and Cu, are known to degrade the minority carrier lifetime (MCL) in semiconducting materials, and maintaining a maximum MCL in heavily doped solar cell Si is of vital importance to realizing a high photovoltaic conversion efficiency.

Because of the large cost differential between single crystal Si wafers and chemically vapor deposited (CVD) polycrystalline Si (polysil) films, sheets, web, ribbons, etc., the latter are more attractive for large area terrestrial solar cell applications. Typical grain sizes in polysil range up to a few tens of microns in films as deposited on metals or graphite, two substrates in common use. The electrical properties of CVD polysil have been investigated, but attempts to incorporate a dopant during the CVD process have not been very successful to date.[4,5] It is believed that the dopant migrates to the grain boundaries during the film deposition process, or that space charge narrowing occurs in the grains due to free carrier trapping at the boundaries. Some dopant atoms may be required in the grain boundaries to neutralize the broken bonds that otherwise would cause space-charge layer widening in the grains, but it has not been possible to obtain a uniform and controlled dopant concentration at the desired dopant concentration level by CVD polysil film techniques to date.[4,5] In CVD polysil, the material remains essentially intrinsic until a certain fraction of the grain boundary bonds are neutralized, and the presence of too many dopant atoms in the grain boundaries may lead to enhanced electrical conduction, thereby decreasing the shunt resistance across a polysil solar cell and reducing the photovoltaic conversion efficiency. Introduction of P into polysil ingots, wafers, or films by neutron transmutation doping offers the obvious advantage of a uniform initial dopant distribution regardless of grain size.

EXPERIMENT

Samples were prepared from commercially available (Texas Instruments Company) high purity (undoped) CVD n-type one-inch diameter polysil rods intended for float zone crystal growth, and three-inch diameter polysil sections intended as crucible charge material for Czochralski growth. The van der Pauw technique was used to determine the donor concentration and mobility, and the photoconductive decay technique (PCD) was used to determine the minority carrier lifetime (MCL). The hydraulic facility of the Oak Ridge Reactor (ORR) and a vertical thimble position in the core of the National Bureau of Standards Reactor (NBSR) were used to introduce an estimated 10^{14} to $\sim 3 \times 10^{16}$ phosphorus cm^{-3} in samples of single crystal Si and polysil at a reactor ambient temperature of ∿ 100°C. The samples were annealed in vacuum for 16-20 hrs at 800°C after irradiation.

RESULTS

Published cross section and reactor neutron flux data were used to estimate the anticipated ^{31}P concentration, and good agreement was obtained between the estimated and measured dopant concentration for al' of the single crystal Si samples. Figure I is a graph of the measured donor concentration vs the predicted donor concentration for typical samples. The solid line indicates the results that were obtained for single crystal Si samples. These data show that neutron transmutation doping can be used to dope this particular type of polysil at any desired donor concentration $\geq 2 \times 10^{15}$ cm^{-3}, and that any impurity migration to grain boundaries cannot be observed as a consequence of annealing up to 800°C. The carrier mobility is much less in this type of polysil than in single crystal Si because of the small grain size, but the mobility increases from ∿ 5 to 50 cm^2 V^{-1} sec^{-1} in these samples when the dopant concentration increases from $\sim 10^{15}$ to 2.8×10^{16} cm^{-3}. The true meaning of a minority carrier lifetime (MCL) in these samples as determined by PCD is not well understood, but the MCL was ∿ 50 μsec for the undoped polysil starting material, and remained at approximately this value for a dopant concentration of $\sim 2.8 \times 10^{16}$ cm^{-3}.

DISCUSSION

Preliminary electron microscope studies indicate that the grain size varies from $\sim$ 1 to 60 microns in the type of CVD polysil used, and that the grains contain dislocations, twins, stacking faults, and defect clusters. It was not anticipated that this type of CVD polysil would be particularly suitable for solar cell fabrication and testing, and these studies will be continued on polysil films as prepared by different techniques such that the grain size and orientation can be controlled and maximized. The fact that the anticipated donor concentration is observed in this material after annealing at 800°C is of special interest in that a p-n junction must be formed to fabricate a solar cell, and preferential migration of dopant impurities along grain boundaries has been predicted for conventional high temperature diffusion experiments. It is anticipated that one can form a p-n junction in NTD polysil film by ion implantation, and that a relatively low temperature (900°C) anneal will remove ion implant damage, without introducing any extensive grain boundary impurity migration. It is also anticipated that one can use neutron transmutation doping to introduce a uniform dopant concentration into Si of any form (ingot, slice, ribbon, web, sheet, or epitaxial layer), either free-standing or as supported or deposited on a suitable substrate (glass, quartz, graphite, Al, or metallurgical grade Si). Polysil starting material of 'solar grade' quality, and certain substrates may contain other impurities, but a reasonable concentration of such impurities can be tolerated, unless their thermal neutron absorption cross section and half-life for radioactive decay are too large to permit subsequent handling after a reasonable period of time. Graphite is used as a reactor moderator material, and certain grades of Al are used for sample containment in many reactor experiments. Controlled doping of an epitaxial layer as deposited on a relatively heavy doped n-type Si substrate (N^+ back layer) is another distinct possibility that is currently under investigation.

SUMMARY

Neutron transmutation doping has been used to introduce a uniform macroscopic and microscopic phosphorus dopant concentration in single and polycrystalline Si, and radiation damage annealing to 800°C does not indicate dopant migration to grain boundaries. Formation of a p-n barrier by diffusion and ion implant techniques is being studied, and controlled doping of an epitaxial layer on a heavily doped Si substrate by neutron transmutation doping is also under investigation.

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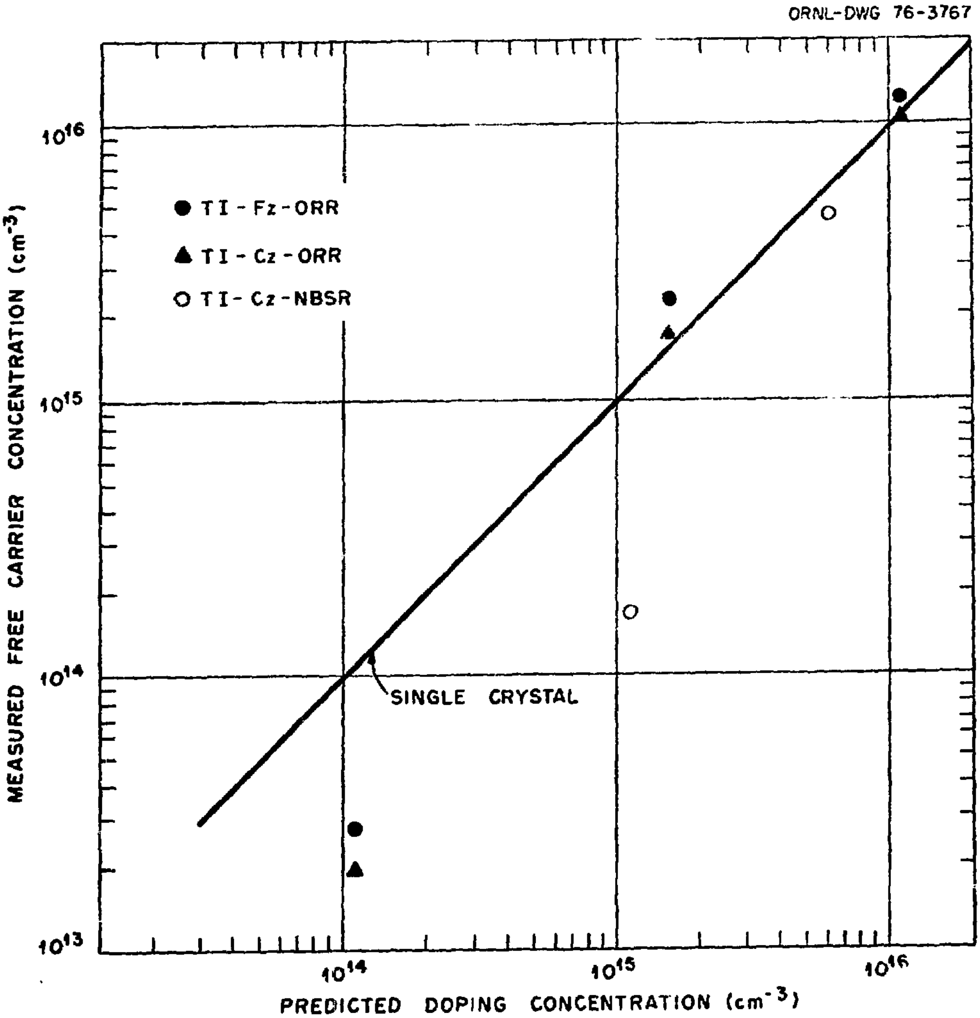

Fig. 1. Graph of the measured donor concentration vs the predicted donor concentration for various samples of neutron transmutation doped (NTD) polycrystalline silicon. The solid line indicates results for NTD-single crystal silicon.