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ABSTRACT

The most promising way to reduce the cost of silicon in solar cells while still maintaining performance is to utilize thin films (10-20 microns thick) of crystalline silicon. The method of solution growth is being employed to grow thin poly-crystalline films of silicon on dissimilar substrates. The initial results indicate that, using tin as the solvent, this growth process only requires operating temperatures in the range of 800°C to 1000°C. Growth rates in the range of 0.4 to 2.0 microns per minute and grain sizes in the range of 20 to 100 microns have been achieved on both quartz and coated steel substrates. Typically, an aspect ratio of two to three between the width and the Si grain thickness is seen. Uniform coverage of Si growth on quartz over a 2.5 x 2.5 cm area has been observed.

TABLE OF CONTENTS

LIST OF FIGURES

I. Introduction

The Silicon-Film process is a method for fabricating solar cells on low-cost substrates. The method is directed to the growth of films of solar cell quality semiconductors on either metallurgical grade (low-cost) semiconductor substrates or on metal substrates. This method is being employed to grow solar cell quality Silicon-Films on metallurgical grade silicon substrates. Solar cell quality layers have been demonstrated on semiconductor grade silicon substrates using a variation of the Silicon-Film process. Epitaxial layers of similar quality using a different growth process have been demonstrated on metallurgical grade silicon by RCA. These RCA-grown layers have resulted in solar cell efficiencies greater than 13%.

Thin film polycrystalline silicon has great potential for achieving low cost. To date, polycrystalline silicon has not been demonstrated with high efficiency in a low cost, thin film configuration. The higher efficiencies for polycrystalline silicon are based on devices made on considerably higher cost substrates.

Thin polycrystalline silicon cells can achieve energy conversion efficiencies close to those demonstrated by single crystal material with the application of advanced optical designs and passivation of the surfaces (including grain boundaries). The maximum performance for any solar cell design can be determined using fundamental material and device parameters. The generalized photovoltaic solar cell is described as having five layers: the opaque electrical contact, the photon-absorber minority-carrier generator, the minority-carrier collector majority-carrier converter, the transparent electrical contact and an anti-reflection coating. An optimized solar cell includes a back suface field, BSF, and a light trapping structure (1).

The calculation of the value for the performance requires the thickness of each layer, the carrier concentration, the minority carrier diffusion length (which varies with the doping level), the absorption coefficient and the surface recombination. The effects of an anti-reflection coating grid reflection, series resistance losses and other losses (which includes contact resistance, shunt effects, etc.) are included (2). Additionally, a light enhancement term (due to light trapping in the silicon) which increases short circuit current has been calculated (3). It has been indicated that this term increases the effective optical thickness of the material up to a factor of 50 for silicon (4). From the analysis, it can be shown that for a polycrystalline Si film thickness of 20 microns, solar cell efficiencies as high as 19.4% can be achieved (5).

The Silicon-Film process is designed to significantly reduce the silicon cost while retaining the physical characteristics of single crystal silicon. The most promising approach for significant cost reduction is the reduction of silicon thickness. Additional cost reductions occur due to the use of a lower cost substrate and the utilization of continuous manufacturing technology.

The principal techniques for growing semiconductors onto foreign substrates are melt growth, vapor phase growth, solid state growth (which is often recrystallization of vapor growth) and solution growth. Several investigators have successfully grown films of silicon from the melt on graphite or graphite-coated ceramics (6,7). These processes offer the advantage of relatively high growth rates. The disadvantages of growing silicon films from the melt are primarily based on the high temperature, 1415°C, which is required to melt silicon. This temperature effectively limits the substrate selection to graphite and ceramics. The potential problems include contamination of the silicon from the substrate and the absolute temperature control required for good crystal growth.

Several techniques for growing from the vapor onto foreign substrates have also been reported (8,9,10). These processes offer the advantage of lower temperatures and acceptable growth rates of several microns per minute. The disadvantages include small grains and contamination of the grains and grain boundaries from the growth medium. The small grain problem has been solved by recrystallization and the contamination problem resolved by growing a new active semiconductor layer from the vapor onto the recrystallized substrates. (9,10). The recrystallization approaches result in relatively thick and highly doped silicon initial layer growth with short diffusion lengths which limit the potential for optical enhancement.

Two hybrid solution growth approaches have been reported. The first deposited silicon from the vapor (in vacuum) on heated aluminum substrates (11). Large grains of silicon were grown from the silicon-aluminum solution which formed. The silicon was saturated with aluminum which led to minority carrier diffusion lengths that were too short for satisfactory solar cell operation. Another approach, chemical vapor deposition of silicon onto heated tin-coated graphite substrates, led to large grain growth from tin solution (12). Apparently, diffusion of impurities from the graphite into the silicon led to unacceptable low minority carrier diffusion lengths.

This work is based on growth from saturated metal solutions. The growth process when performed on similar or lattice matched substrates is called liquid phase epitaxial growth. Liquid phase epitaxy will, in general, produce material that forms devices that are superior in performance to those grown by other methods (13). These superior performance devices include light emitting diodes, semicondcutor lasers, magnetic garnet bubble memories and

GaAs solar cells. The improved performance of liquid phase epitaxial devices, when compared to vapor phase or diffused devices, can be attributed to the exact stoichiometry control, longer diffusion lengths, fewer deep levels and the tendency of impurities to segregate to the liquid rather than the solid. Liquid phase epitaxy also has the tendency to anneal out dislocations in the substrate.

A general procedure for the analysis of crystal growth from solution has been described (14). For a good quality crystalline overlayer on a substrate, the growth process can be separated into the following four steps: 1) wetting, 2) nucleation, 3) non-impinging crystal growth and 4) film crystal growth. The division of this generalized procedure into its four component parts leads to a more comprehensive analysis of each of the required steps. These four steps will be discussed and illustrated in the Technical Discussion section which follows.

Growth from saturated solutions for the growth of solar cell quality silicon on metal and glass substrates offers the advantages of low growth temperature, demonstrated large grain growth, long minority carrier diffusion lengths and the potential for annealing out some of the strains and dislocations caused by the dissimilar substrates. Some disadvantages are that this process has not been previously demonstrated on dissimilar substrates and that high through-put manufacturing technology has not been demonstrated.

II. Technical Discussion

Tin has been employed as the solvent for silicon since long minority carrier lifetimes can be maintained in silicon saturated with tin. Solar cells grown from saturated tin solutions onto silicon substrates have been reported (15). The semiconductor-film process has been used to grow silicon onto 0.010 inch thick steel and 0.040 inch thick quartz substrates. The steel has been coated with silicon carbide to provide a metallurgical barrier. The quartz was also covered with silicon carbide. Growth temperatures in the range of 800°C to 1000°C were used for silicon growth. Both ramp cooling at 0.1° to 3°C per minute and steady state growth techniques with a temperature gradient (16) between 10° and 100° C per centimeter were used. Growth rates for silicon ranged from 0.5 to 4 microns per minute.

Wetting, which relates to the bonding between the nutrient medium and the substrate, plus between the crystalline semiconductor and the substrate, has been accomplished on both steel and quartz substrates.

Nucleation, which relates to the formation step of semiconductor crystallites on the substrate, has also been achieved on both the steel and quartz substrates. Nucleation needs to be well controlled so that the crystal initiation and the crystal growth steps may be separated.

Non-impinging crystal growth relates to the initial stages of growth of the crystals produced by the nucleation step. The growth rate of the crystals is determined by the flux of semiconductor from the nutrient medium across the convection free boundary layer at the crystal/medium interface. The growth of non-impinging silicon grains on quartz and steel are shown in Figure 1. The silicon grains on quartz are 49 microns tall and 104 microns wide on 120 micron spacing. The silicon grains on steel are 48 microns wide and 33 microns thick with 140 micron spacing.

Figure 1

a) Silicon Crystals
   on Quartz
   1.3 mm x 1.0 mm
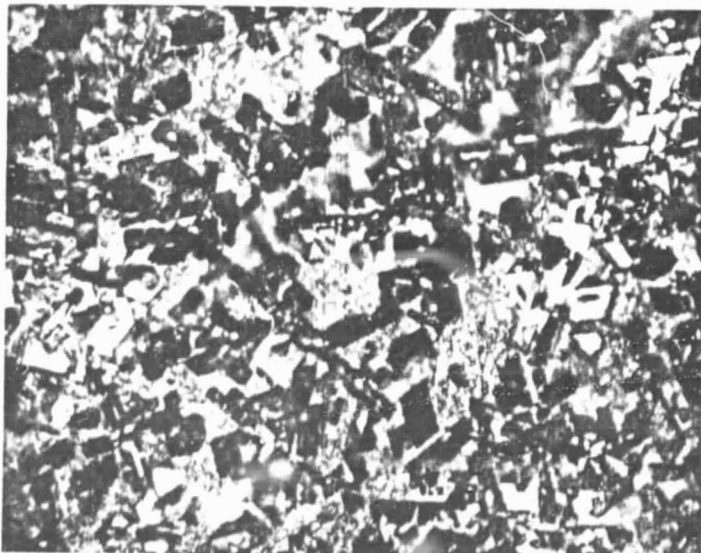
b) Silicon Crystals
   on Steel
   1.3 mm x 1.0 mm

Film crystal growth relates to the final stage of crystallite growth after the peripheries of adjacent crystallites have begun to closely approach and touch each other. At this stage, the film is comprised of a set of scallop-shaped crystallites on the substrate. The semiconductor flux to these impinging crystallites must be reduced so as to allow nutrient and impurities trapped in the grooves to diffuse back to the bulk medium. Control of the nutrient and the interface can lead to a relatively planar growth surface with benign boundaries. Silicon-films on quartz and steel are shown in Figure 2. Continuous silicon-films on quartz for areas greater than one square centimeter have been demonstrated. Film thickness of twenty microns plus or minus 10% have been achieved. Silicon-films on steel have demonstrated dendritic growth with incomplete fill-in between the dendrites. One square millimeter films 50 microns thick have been grown.
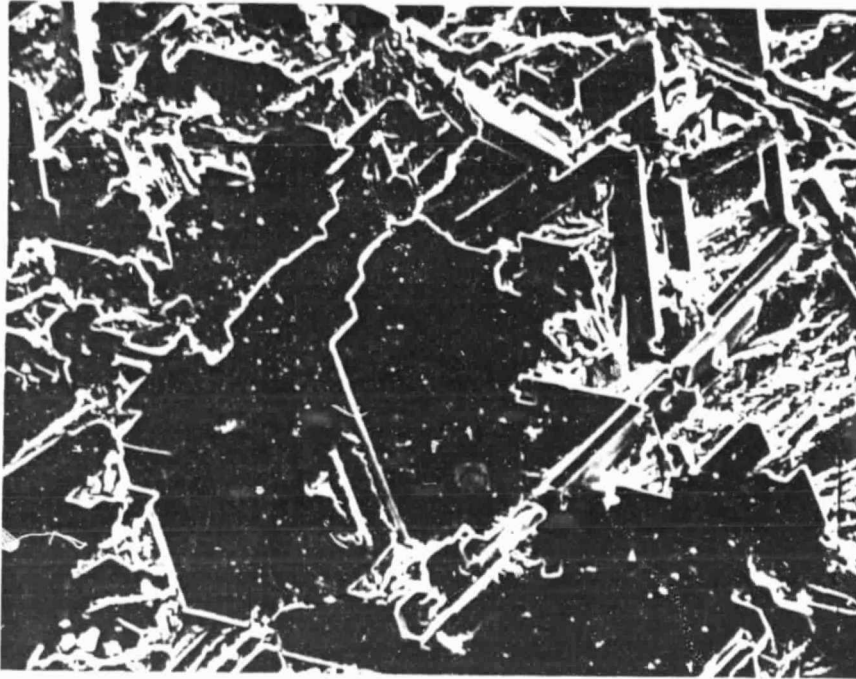
Figure 2
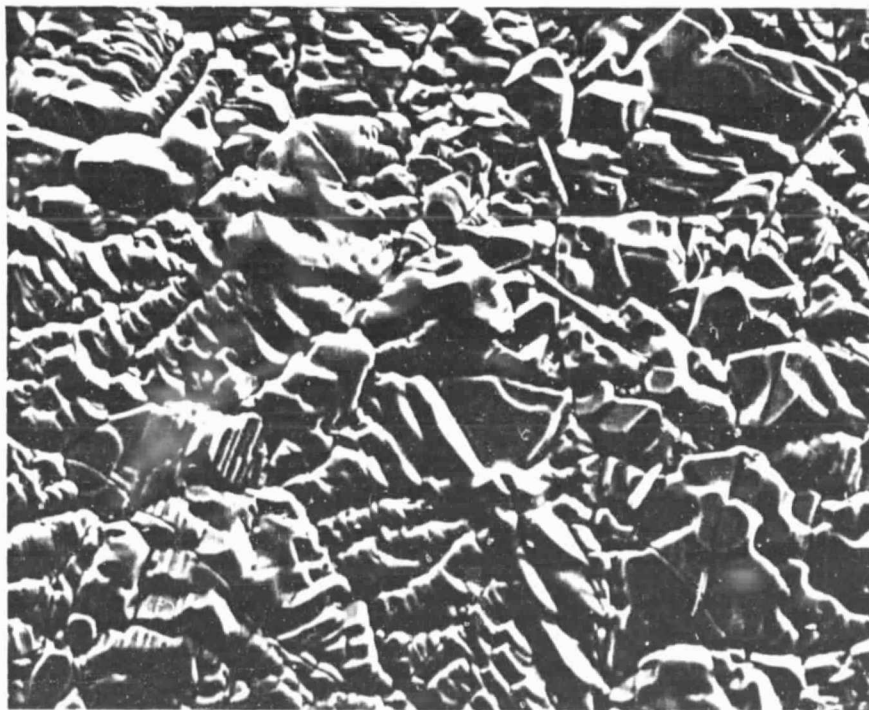
a) Silicon-Film on Quartz
0.71 mm x 0.54 mm

Figure 2

b) Silicon-Film on Steel
0.71 mm x 0.55 mm

The composition of a grown layer of silicon steel was
determined by EDAX to be silicon with a trace of tin; the
data are shown in Figure 3.

III. Conclusions

The initial results have demonstrated all phases of the Si
growth process on steel and quartz using the solution growth
technique. The growth achieved to date are typically 20-70
microns high with aspect ratios (width to height) of two to
three for individual grains.

Figure 3

26-MAR-84 01:23:14 EDAX READY
RATE: 3071CPS TIME: 100LSEC
00-20KEV:10EV/CH PRST   100LSEC
A:EXP 009 AREA 3B:
FS=   3654   MEM: A   FS=   50

CURSOR (KEV)=03.860   EDAX
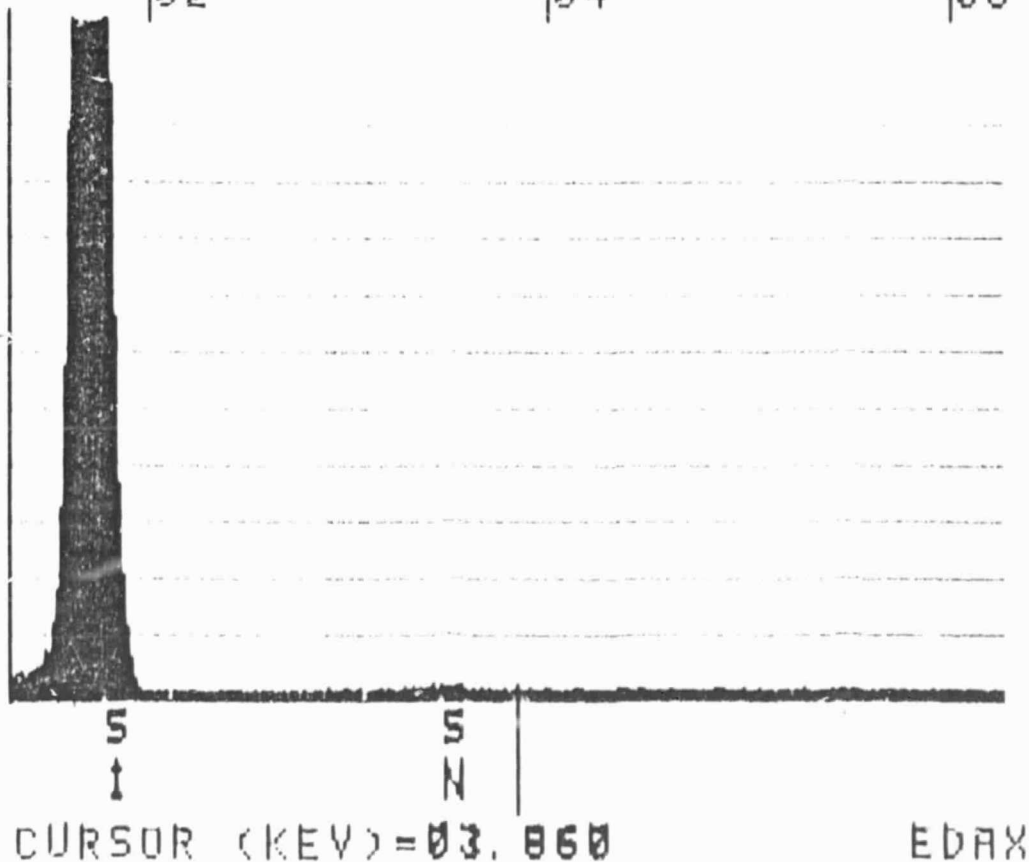
EDAX of Silicon-Film on Steel

IV. Work Planned

During the next quarter, work will continue on quantifying the growth steps. Growth runs directed toward the achievement of uniform and complete Si-film growth over two square centimeters will be conducted. Experiments will be performed to examine the minority carrier diffusion length of these films.

V. New Technology

A. Growth of polycrystalline Si on quartz and coated steel using solution growth.

A. M. Barnett, R. B. Hall and J. B. McNeely are the innovators of this technology which is being initially disclosed on the date of this report, pages 1 through 8 .

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