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Studies of the Nature of Interfacial Barriers in High Efficiency Crystalline Silicon Solar Cells.

FINAL REPORT

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STUDIES OF THE NATURE OF INTERFACIAL BARRIERS
IN HIGH EFFICIENCY CRYSTALLINE SILICON SOLAR CELLS

I. PROGRAM AS A WHOLE

The program was a one year effort to study the effects of interfacial barriers in crystalline silicon solar cells. And as specified in the work statement the effort was directed toward the investigation and use of such techniques as Angular Resolved Auger Parameter Spectroscopy (ARAPS) and Impedance Spectroscopy in initially characterizing n-type Si doped to levels commonly used for n^+p solar cells, and eventually Si solar cells supplied by JPL.

In the performance of this effort Stanford University was supposed to:

1. Procure the necessary equipment for impedance measurements and establish capability comparable to that presently used at Stanford Research Institute.

2. Investigate the chemical structure of SiO_2/Si interfaces with ARAPS for n-type Si having carrier concentrations greater than $10^{18} cm^{-3}$.

3. Measure the complex impedance so as to determine the interface state density throughout the bandgap for SiO_2/Si interfaces and relate with non-stoichiometric configurations or impurities found in the SiO_2 layer by ARAPS.

4. Provide all data and four (4) samples of SiO_2/Si, which have been characterized by techniques outlined in paragraphs (2) and (3), for independent measurements of surface recombination velocity.

5. Extend the ARAPS and Impedance Spectroscopy techniques to no more than twelve (12) samples of Si interfaces with passivating layers of SiN_x or other dielectrics.

6. Improve SiO_2/Si interface properties so as to reduce surface recombination velocity by process optimization, using the density-of-states measured by impedance spectroscopy as a measure of improvement and establish relationships between SiO_2/Si, SiN_x/Si, or other interfaces and surface recombination velocity.

7. Provide personnel to support Project Integration Meetings and Program Review Meetings.

Tasks (1) and (7) were accomplished as a matter of routine compliance. However, between the start of the contract and the delivery of the Solartron Measurement System there was a six months interval. An additional two weeks were required to set up the equipment to begin data taking. As the X-ray photoelectron spectrometer was already operational work was immediately started on task (2) and the vast amount of work accomplished using XPS is a partial reflection of that (XPS is an acronym for x-ray photoelectron spectroscopy). However five and one half months were left to accomplish tasks (3), (4), (5) and (6) - a fairly unrealistic amount of time. The work effort was restructured to provide

the most meaningful information with the limited time and funds available. One of the major criticisms of the program as a whole is that too much was asked to be done in one year. The contract should have been for at least two years or more.

II. MAJOR ACCOMPLISHMENTS

In this section instead of just listing the major accomplishments from this one year effort, those tasks that were completed in section I will be indicated and the major accomplishments noted. (1) and (7) were completed.

Task (2) was accomplished and the work performed contributed to an understanding of SiO_2/Si interfaces that was previously lacking and is considered a major accomplishment. The results of this study have been published (Appl. Phys. Lett.47 (10) 1064 (1985)) and only an outline of this work is presented here.

Initial state effect is a measure of the valence charge density around the atom and is influenced by changes in the atomic oxidation state. For $Si-SiO_2$ system the initial state effect may be examined using XPS by taking the difference in the kinetic energies of the core level $Si2p(SiO_2)$ and $O1s$ (SiO_2) peaks. The 2p and 1s designations are the usual one electron orbital state designations. The electrostatic charging effects and the matrix effects cancel out because the difference in energies is taken for two elements in the same medium. Table I lists the $\Delta E(Si2p-O1s)$ for 13 to 200Å thick SiO_2 grown over Si, fused silica,

and two crystalline polymorphs of SiO_2, namely α-Quartz α-Cristobalite. Note $\Delta E(Si2p-O1s)$ is the same i.e., 429.7eV for all the samples in Table I. These data show that the thermal oxide is chemically uniform at least up to 13Å from the interface and is also chemically the same as the bulk forms of SiO_2. Note that $\Delta E(Si2p-O1s)$ for α-Quartz having a Si-O-Si bridging bond angle of 144° is equal to that of α-Cristobalite having a Si-O-Si bridging bond angle of 148±1°. It has been proposed by Grunthaner and co workers that the strain in SiO_2 near the Si-SiO_2 interface leads to a change in the charge transfer in Si-O bond due to a variation in Si-O-Si bond angle. Our results indicate that this structure induced charge transfer effect is rather small (<0.1eV).

Final state effect in the Si-SiO_2 system can be examined by analyzing the core level Auger parameter for Si. Auger parameter, α is defined as:

$$\alpha = KE_{Auger} \text{ minus } KE_{photoelectron} \tag{1}$$

where
$$KE_{Auger} = \text{Kinetic energy of the Auger peak}$$
$$KE_{photoelectron} = \text{Kinetic energy of the photoelectron peak}$$

The Auger parameters for Si in SiO_2, $\alpha_{Si}(SiO_2)$ and in substrate Si, $\alpha_{Si}(Si)$ were determined by measuring the kinetic energies of Si KLL and Si2p peaks. Auger parameter provides a measure of the screening energy of the medium surrounding the core hole. It is independent of the electrostatic charging effects and the energy referencing. Table I shows

$\alpha_{Si}(SiO_2)$ for thermal oxides on Si ranging in thickness from 13 to 200Å, and for the SiO_2 polymorphs. Lack of any significant variation for $\alpha_{Si}(SiO_2)$ among thermal oxides and between thermal oxides and between SiO_2 polymorphs shows that the screening energy at the $Si-SiO_2$ interface is essentially equal to that in bulk SiO_2. The basic structural unit for all forms of crystalline and amorphous SiO_2 is the SiO_4 tetrahedron and the intertetrahedral (Si-O-Si) angle defines the various forms of SiO_2. So Si nearest-neighbors for all forms of SiO_2 are the same. Linking this observation with the results on the Auger parameter for Si, it is concluded that the screening energy is provided predominantly by the Si nearest-neighbors and the long range screening effects in SiO_2 and in Si are negligible. This result supports the Grunthaner et al.'s observations but differs with Wagner's conclusions.

The above conclusion is also supported by considering the thermodynamics of SiO_2 formation. The standard Gibbs free energy of formation, ΔG_f° for SiO_2 is partitioned by the following defining equation into enthalpy of formation, ΔH_f° and entropy of formation ΔS_f°.

$$\Delta G_f^\circ = \Delta H_f^\circ - T\Delta S_f^\circ \qquad (2)$$

Equation 2 provides a measure of the relative contribution to the driving force for SiO_2 formation. Comparing values of ΔH_f° and $T\Delta S_f^\circ$ from thermochemical tables for α-Quartz, α-Cristobalite, β-Cristobalite it is found that 94% of the driving force is due to enthalpy and only 6% is due

to entropy. Clearly most of the driving force is consumed in forming SiO_4 tetrahedron and only 6% of the driving force is used in varying Si-0-Si bond angle. Hence the thermodynamic data emphasizes the dominant role played by Si nearest-neighbors and lends credence to the earlier conclusion that the structure induced charge transfer effects are rather small.

T A B L E   I

S A M P L E	EXIT ANGLE	ΔE(Si2p-01s) (eV)	AUGER PARAMETER, α (eV)	
			$\alpha Si(SiO_2)$	$\alpha(Si)$
13Å SiO_2/p-Si (800°C)	15°	429.7	225.6	229.3
	60°	429.7	225.5	229.3
23Å SiO_2/p-Si (800°C)	15°	429.7	225.4	229.4
	60°	–	225.4	229.4
50Å SiO_2/p-Si (800°C)	15°	429.7	225.3	229.4
	45°	429.7	225.3	229.3
50Å SiO_2/p-Si (1000°C)	15°	429.8	225.4	229.3
	45°	429.8	225.4	229.3
90Å SiO_2/p-Si (1000°C)	15°	429.7	225.3	229.4
	45°	429.7	225.3	–
120Å SiO_2/p-Si (1000°C)	15°	429.7	225.3	–
	45°	429.7	225.3	–
200Å SiO_2/p-Si (1000°C)	15°	429.7	225.3	–
	45°	429.7	225.3	–
α-Quartz	15°	429.7	225.5	–
	45°	429.7	225.5	–
α-Cristobalite	15°	429.7	225.2	–
	45°	429.7	225.2	–
Fused Silica	15°	429.7	225.2	–
	45°	429.7	225.2	–

Task (3). The Si-SiO$_2$ interface was examined by Impedance Spectroscopy (IS). IS data taken over a frequency range from 10 mHz to 10 MHz allows determination of slow and fast interface states. Unfortunately the samples from JPL did not meet the requirements for analysis because IS requires an MIS (Metal-Insulator-Semiconductor) structure but the JPL samples had a p/n+ junction in series with the MIS structure. Consequently in the forward bias case the total capacitance was dominated by the current (i) through the sample

$$i = C \frac{dv}{dt}$$

In the reverse biased case the total capacitance was dominated by the junction capacitance. Both these cases prevented probing of the n+/SiO$_2$ interface and thus we were unable to determine the interface state density could not be determined under those conditions. However a simple temperature cell in which the sample could have been cooled continuously from room to liquid nitrogen temperatures would have provided a means for getting around the high carrier concentration limitation. This was not attempted because of time limitations.

Task (4). This task was not attempted because of the lack of total success for task (3).

Task (5). Examination by XPS was made of the CVD films of Silicon Oxyritnides (SiO$_x$N$_y$). It was found that Si in SiO$_x$N$_y$ is bonded in a complex way to O and N. The film was depth profiled by angle-resolved

XPS and a gradient was observed in O and N concentration from the surface to the bulk of the film. The results showed that the surface of the film is enriched with O and is depleted of N.

The results on Si-SiO$_2$ and Si-SiO$_x$N$_y$ systems show that XPS is a useful tool in examining bonding configurations and also in determining the composition and the concentration profiles in these films. XPS can be used in an effective way to monitor the effects of CVD processing parameters on film stoichiometry and microstructure. This was an important result.

Task (6). This was not attempted because of lack of time.

III. RECOMMENDATIONS

There are just two recommendations to be made involving this work.

1. Extend the impedance spectroscopy measurements to liquid nitrogen temperatures to overcome the high carrier concentration obtained at room temperature.

2. Use XPS and ARAPS to monitor film structure of SiN$_x$ passivating layers.