SIPOS HETEROJUNCTION CONTACTS TO SILICON

Young H. Kwark, Ron Sinton, Richard M. Swanson

110 McCullough Building, Stanford Electronics Laboratories
Stanford, CA. 94305 (415)497-0503

Abstract: Using SIPOS films (SiO_x, x <2) as an emitter contact has been previously shown to reduce the emitter saturation current, J_{oe}, by at least a factor of fifty when compared to a conventional emitter structure with a metallic contact. Previous attempts to explain this J_{oe} reduction have focused on the bulk properties of the SIPOS films. Experimental results of this study which attained J_{oe} values of $2 \times 10^{-}14$ A/cm^2, suggest that an interfacial layer between the SIPOS and underlying silicon may play an important, if not dominant, role with the implication that the high oxygen concentrations previously used may not be essential for J_{oe} reduction. This would permit the use of lower oxygen content SIPOS films whose lower bulk resistivities would allow utilization of these films in structures such as scaled VLSI bipolar devices and high concentration point contact solar cells where series resistance is detrimental to device performance.

Introduction: Deliberate introduction of controlled amounts of an oxygen bearing species such as nitrous oxide into the deposition ambient normally used for chemical vapor deposition of polysilicon produces SIPOS, a class of silicon oxides which exhibits a wide range of physical properties (1). It is possible to tailor film characteristics such as the refractive index, by altering the oxygen partial pressure in the deposition ambient. The addition of a dopant species converts these films from semi-insulating to a form that can be made sufficiently conductive after annealing to make them interesting for electronic applications (2). Incorporation of these films into the emitter structure of an NPN bipolar transistor had been found to reduce the emitter saturation current fifty fold (3); this translates into potential improvements of energy conversion efficiency for solar cells and enhanced high frequency performance of bipolar structures.

Matsushita (3) hypothesized that large amounts of oxygen in his SIPOS films produce a bandgap larger than for monocrystalline silicon. In N-type SIPOS emitter contacts the lining up of the equilibrium Fermi levels results in a barrier in the valence band which blocks hole transport and accounts for the reduction in J_{oe}. Simplified density of states calculations using small clusters of SiO_x lend qualitative support to this scenario; namely the gap in the density of states increases in a continuous manner as the oxygen content in SiO_x is increased (4). However, it is important to note that these clusters were constructed assuming a uniform and random distribution of oxygen throughout the film. While this may apply to films prepared at low temperatures (e.g. evaporation or sputtering), the CVD deposited SIPOS films used in these devices require a high temperature anneal in order to activate the dopant. A phase precipiation which results in a fine dispersion of silicon microcrystallites embedded in an oxygen rich matrix appears to be the result of such anneals (5). Such a heterogeneous structure would indicate that a model based on an effective bandgap and diffusion length may be oversimplified.

Experimental Results: Bipolar test structures and measurement techniques were refined to allow measurement of the emitter saturation current at these low levels; a sample Gummel plot showing the area related component from which J_{oe}, the emitter saturation current, was extracted is shown in Fig. 1. Devices with differing area/perimeter ratios were used in conjunction with the definition

$$I_{base} = Area * J_{area} + Perimeter * J_{peri}$$

to effect this separation. By utilizing various SIPOS emitter contact configurations, these measurements, after correcting to 300°K, allowed determination of which film parameters were relevant in determining the hole blocking action of the films.

The first set of experiments investigated the effect of varying the oxygen content on J_{oe}. These films were deposited in a hot wall APCVD reactor using nitrogen as the carrier gas. Varying γ, the ratio of nitrous oxide to silane in the deposition ambient, from $\gamma = 0$ (which should produce POLY) to $\gamma = 1.5$ (which should produce films comparable to ref. (3)) should display a monotonically decreasing J_{oe} as hole transport is increasingly impeded by the increasing bandgap in the bulk SIPOS. In fact for devices annealed at 900°C/13 min, there is very little dependence on γ as seen in Fig. 2, although increasing the anneal temperature to 1000°C adversly affected J_{oe}. That the γ=0 films produced such good results was surprising since POLY films of comparble thickness should yield a J_{oe} an order of magnitude larger. In fact it was discovered that these $\gamma = 0$ films

32.2

CH2099-0/84/0000-0742 $1.00 © 1984 IEDM

Authorized licensed use limited to: Sidley Austin LLP. Downloaded on March 26,2024 at 22:45:30 UTC from IEEE Xplore. Restrictions apply.

incorporated significant (several atomic %) amounts of oxygen as indicated from electron microprobe and the fact that they etched, albeit slowly, in buffered HF. This insensitivity to bulk film properties implies that other mechanisms, in this case the formation of an interfacial oxide layer as a result of the annealing process (Fig. 3), may be primarily responsible for the reduced hole currents. This conclusion suggests that the mechanism of hole suppression is akin to that for polysilicon SIS contacts, and that the distinguishing feature of SIPOS may be its built-in source of oxygen which aids in the formation and/or maintainence of this interfacial layer.

In order to establish unambiguous results for a relatively oxygen free film, POLY films doped insitu in an RF heated cold wall APCVD reactor using a hydrogen carrier were used in the next set of emitter contacts; these films did not etch in BHF. Fig. 4 displays the resulting J_{oe} as a function of annealing temperature for emitter B which had a Gaussian (3×10^{19} surface concentration, 1 micron depth into 5×10^{16} background) emitter diffused prior to the POLY deposition and emitter C which relied solely on outdiffusion from the doped POLY to form the base-emitter junction. For both structures, devices were prepared with and without a chemically grown oxide (chemox) by dipping half of the wafer which underwent a full RCA clean in dilute HF. The value for emitter B with a conventional aluminum contact is shown for reference. Addition of POLY without the chemox does not greatly impact J_{oe} as would be expected since the heavily doped POLY acts essentially as an extension of the monocrystalline emitter. Addition of the chemox greatly decreases the J_{oe} as has been previously reported (6). "Prediffused" emitter B displays a baseline J_{oe} of 5×10^{-14} A/cm^2 due to recombination in the bulk of the emitter. To this is added a component due to outdiffusion from the heavily doped POLY which becomes increasingly significant for annealing temperatures above 900°C. This is apparent if one notes that the increase in J_{oe} for emitter B can be accounted for by the J_{oe} of emitter C at the same temperature. At 1000°C, this outdiffusion is severe enough to dominate the J_{oe} which accounted for the lack of difference between emitters B and C.

In Fig. 5, J_{oe} for a $\gamma = 0$ SIPOS film (which recall has several at% oxygen) without the chemox is shown. The behavior above 850°C strongly resembles the POLY case with chemox. Addition of the chemox to the SIPOS contact structure does not greatly affect the lowest values of J_{oe} attained. However, the increase in J_{oe} at higher temperatures is not as severe as for the devices in Fig. 4 and 5. Furthermore, devices annealed at 850°C, while displaying the same J_{oe} as the SIPOS devices without the chemox, also suffered from greatly increased series resistance.

Discussion: Emitter saturation currents of $1 - 2 \times 10^{-14}$ A/cm^2 have been attained for POLY with chemox and for both SIPOS contact structures. That there was little difference in J_{oe} between the SIPOS contacted emitters with and without the chemox would indicate that the interface between SIPOS and monocrystalline silicon is similar in both cases. Postulating the formation of a thin tunnelable interfacial oxide as a consequence of the high temperature annealing step is consistent with the observed similarities in J_{oe}. The smaller increase in J_{oe} for the SIPOS device with chemox can be explained by assuming that the chemox simply adds an additional thickness to the oxide layer resulting from the anneal step. This would act as a more robust diffusion barrier and would limit the extent of outdiffusion of dopants from the SIPOS thus reducing bulk recombination in the monocrystalline emitter region. This is also consistent with the increased series resistance which would arise from a thicker interfacial layer. The possibilty remains that a thin thermal oxide is growing during the thermal equilibration phase prior to deposition of the SIPOS films; although standard precautions were taken to minimze the presence of oxygen and water vapor in the deposition ambient, the apparatus currently available can not be used to rule out this possibility.

A key figure of merit which has not been discussed is the specific resistivity of the emitter contact structure. For the SIPOS films mentioned in ref. (3), a specific contact resistivity of 1×10^{-3} ohm-cm^2 would result for a 1000 angstrom thick film. This is far too high to permit use in scaled bipolar or in high concentration point contact solar cells. If the hole barrier mechanism operative in SIPOS contacts is indeed associated with the formation of interfacial layers, then there is no apriori need for such high oxygen concentrations in the bulk of the films with their attendant high resistivity. The focus, in this case, would shift to the kinetics of the annealing process and to the morphology of the near interface region, much as is the case with POLY SIS structures. For the $\gamma = 0$ SIPOS contacts, an upper limit to the specific resistivity can be set at 1×10^{-4} ohm-cm^2 from device Gummel plots; although the actual value is quite likely to be far below this, the presence of other parasitic resistances does not allow a more refined determination from the device data. The ability to directly measure the voltage drop at the interface is being incorporated into the next mask set.

References:

(1) D. Dong, E. Irene, et al "Preparation and Some Properties of CVD Si-rich SiO_2 and Si_3N_4 Films", J. Electrochemical Soc. 125(5), May 1978, p819

(2) H. Yamoto, N. Oh-uchi , et al "New Technology by the Use of Doped SIPOS Films", ECS Abstracts, #168, 1979

(3) T. Matsushita, "A Silicon Heterojunction Transistor," Appl. Phys. Lett., vol 35(7), p 549, 1979

(4) A. Bennet, L. Roth "Calculation of the Optical Properties of Amorphous SiO_x Materials" Phys. Rev. B 4(8), Oct. 15, 1971, p 2686

(5) M. Hamasaki, "Crystallographic Study of SIPOS Doped with Oxygen Atoms,"J. Appl. Phys. 49(7), p 3987, 1978

(6) B. Soerowirdjo, P. Ashburn, et al "The Influence of Surface Treatments on the Electrical Characteristics of Polysilicon Emitter Bipolar Transistors" Tech. Digest IEDM, 1982, p 668

Authorized licensed use limited to: Sidley Austin LLP. Downloaded on March 26,2024 at 22:45:30 UTC from IEEE Xplore. Restrictions apply.

Petitioner Canadian Solar (USA) Inc., Ex. 1024, p. 743

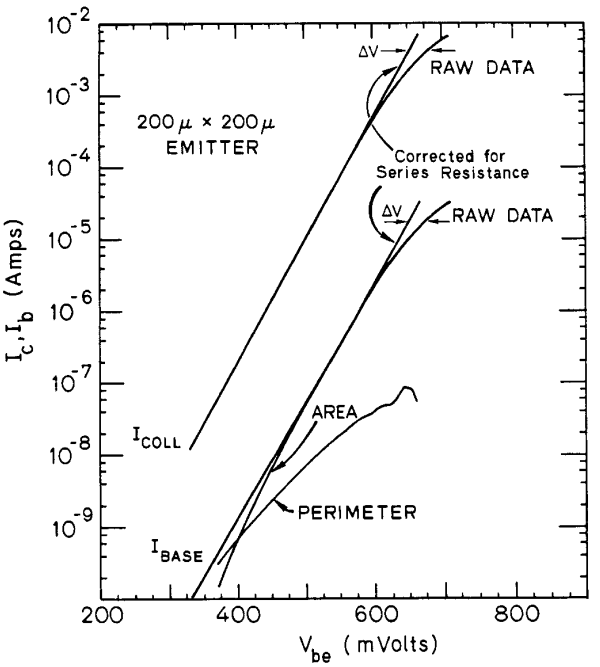

Fig. 1: Gummel plot of test bipolar structure showing area and perimeter related components.

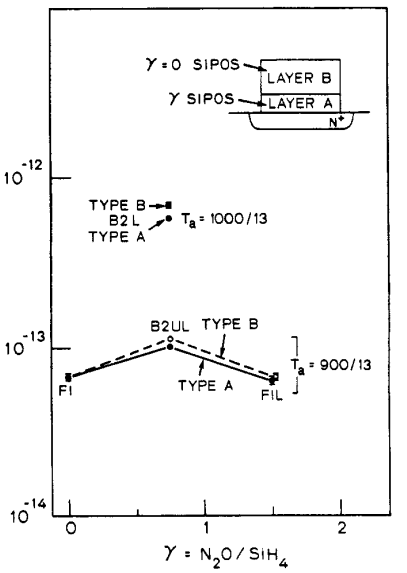

Fig.2: γ is the ratio of nitrous oxide to silane in the SIPOS deposition ambient, T_a is the anneal temperature (followed by a slash and anneal time in minutes). Layer B is a 2000 angstrom capping layer; layer A is the "active layer" ranging from 1000 to 1600 angstroms.

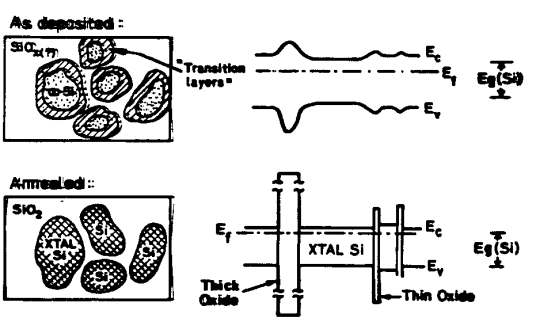

Fig. 3: (A) postulated structure of as-deposited SIPOS (B) and after annealing; the "oxide-like" regions become more SiO_2-like, accompanied by crystallization of the silicon crystallites.

32.2

Authorized licensed use limited to: Sidley Austin LLP. Downloaded on March 26,2024 at 22:45:30 UTC from IEEE Xplore. Restrictions apply.

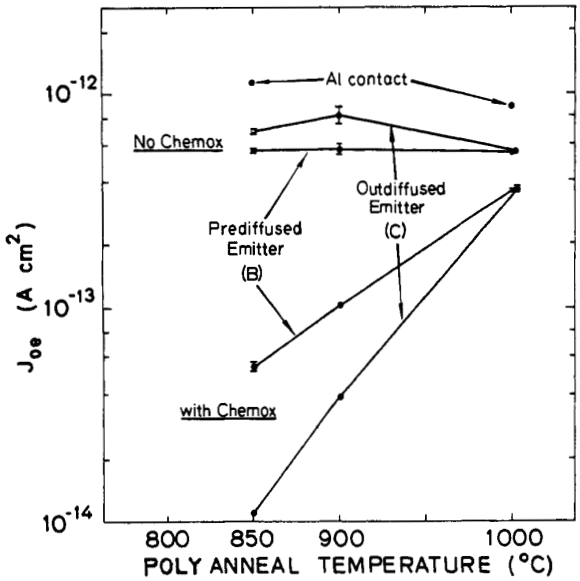

Fig. 4: emitter saturation current for POLY contacts with and without a chemically grown interfacial layer vs. anneal temperature. Thicknesses range from 3000-3600 angstroms. Note the large difference when the interfacial oxide is missing.

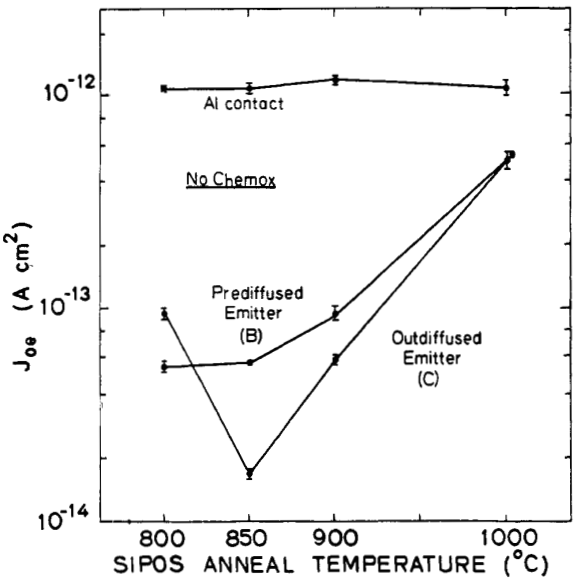

Fig. 5: emitter saturation current vs. anneal temperature for SIPOS contacts without a chemically grown interfacial oxide. The $\gamma = 0$ SIPOS layer is 3300 angstroms thick.

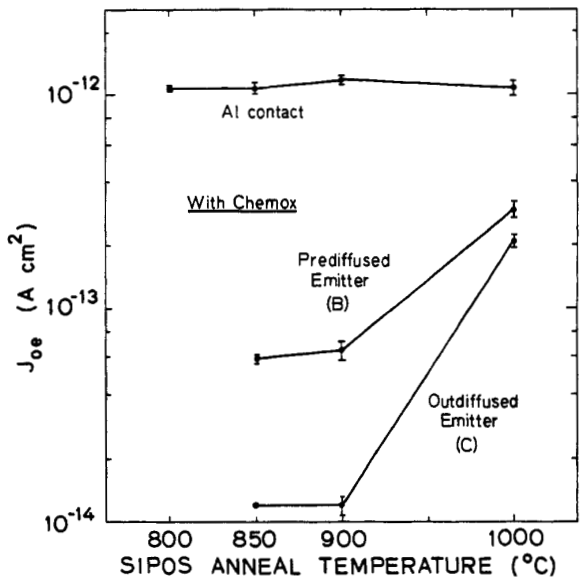

Fig. 6: emitter saturation current vs. anneal temperature for SIPOS contacts with a chemically grown interfacial oxide. The $\gamma = 0$ SIPOS layer is 3300 angstroms thick.

Authorized licensed use limited to: Sidley Austin LLP. Downloaded on March 26,2024 at 22:45:30 UTC from IEEE Xplore. Restrictions apply.

Petitioner Canadian Solar (USA) Inc., Ex. 1024, p. 745