

The effect of chlorine on dopant activation in hydrogenated amorphous silicon

Adam M. Payne^{a)} and Sigurd Wagner

Department of Electrical Engineering, Princeton University, Princeton, New Jersey 08544

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The dark conductivity of hydrogenated amorphous silicon (*a*-Si:H) films deposited from dichlorosilane (SiCl_2H_2) and silane (SiH_4), and doped with diborane (B_2H_6), increases by as much as a factor of 100 over the usual *a*-Si:H,B films deposited without SiCl_2H_2 . The effect is observed at gas phase concentrations of diborane ranging from 0.006 to 0.5 vol %, and for both direct current (dc) and 13.56 MHz radio frequency plasma depositions, although it is more noticeable for the dc discharge. An increase in dark conductivity is also observed in boron doped hydrogenated amorphous silicon carbon alloys (*a*-SiC:H) deposited with dichlorosilane, albeit coupled with a change in the Tauc gap. Chlorine reduces the conductivity of undoped and phosphorus doped *a*-Si:H films. A B-Cl cluster acceptor that is not passivated by H is proposed as a possible mechanism for chlorine enhanced conductivity. This increase in *p*-layer conductivity translates into an increase of solar cell efficiency, but surprisingly by an increase in photocurrent rather than open circuit voltage. © 2000 American Institute of Physics. [S0003-6951(00)02120-3]

Hydrogenated amorphous silicon (*a*-Si:H) is used commercially in solar cells and thin-film transistors. One limitation of the electronic performance of these devices is imposed by the limited doping efficiency of phosphorus and boron in *a*-Si:H, so an enhanced doping efficiency is much desired.¹ As part of our work on using dichlorosilane (SiCl_2H_2) to deposit *a*-Si:H with an increased deposition rate we have deposited *a*-Si:H films using SiH_4 and SiCl_2H_2 mixtures with PH_3 and B_2H_6 to investigate the properties of doped films with and without chlorine.

The first clue that chlorine could have an effect on doping occurred in earlier work. Amorphous silicon *p-i-n* solar cells deposited using a $\text{SiCl}_2\text{H}_2/\text{SiH}_4$ mixture for the *i* layer had reduced open circuit voltage V_{oc} when the chlorinated layer was adjacent to the *n* layer.² This reduction was reversed by interposing a thin interfacial layer deposited using only silane. To investigate this loss of V_{oc} we grew phosphorus doped films, from mixtures of SiH_4 and PH_3 with and without SiCl_2H_2 as well as undoped films for controls. These films were grown under identical deposition conditions except for the addition of dichlorosilane ($T_{\text{substrate}} = 300^\circ\text{C}$, deposition pressure 500 mTorr (62 Pa), dc and rf (13.56 MHz) excitation, power density $\sim 75\text{--}100\text{ mW/cm}^2$, 50 or 47 sccm SiH_4 , 0 or 3 sccm SiCl_2H_2 , and 1 vol % PH_3 in H_2 at 6 sccm). In addition boron-doped films were also deposited under the same conditions, substituting 1 vol % B_2H_6 in H_2 which varied from 0.3 to 50 sccm for PH_3 and a substrate temperature of 260°C . Adding the SiCl_2H_2 tends to lower the dc discharge voltage, therefore lowering the power slightly, but the deposition rates were unchanged at $\sim 4\text{--}5\text{ \AA/s}$. We expanded the investigation of the boron-doped *a*-Si:H films to include films of boron-doped amorphous silicon carbon alloys (*a*-SiC:H) to identify any effect of the enhanced conductivity on the *p* layer of typical solar cells.

Deposition conditions were the same as the dc deposited boron-doped *a*-Si:H films described above except that the following flow rates were used: 4.5 sccm CH_4 , 41 (40) sccm SiH_4 , 0 (3) sccm SiCl_2H_2 , and 5 sccm 1 vol % B_2H_6 in H_2 .

Coplanar thermally evaporated aluminum electrodes 7.5 mm long with a gap of 0.5 mm were used to determine the thermal activation energy of the dark conductivity in the range between room temperature and 110°C . Optical transmission spectra were evaluated to determine the film thickness and absorption coefficient from which the Tauc gap was calculated. Solar cells were fabricated using the B-doped *a*-SiC:H films as the *p* layers on Solarex textured SnO_2 coated glass substrates with a structure of 13–26 nm *p* layer/8 nm buffer layer (*a*-SiC:H)/500 nm *i* layer (*a*-Si:H)/18 nm *n* layer (*a*-Si:H). Aluminum 0.25 cm^2 back contact squares were deposited by thermal evaporation followed by a 60 min anneal at 120°C in air at 1 atm. The front contact was indium solder and multistrand copper wire. The current-voltage characteristics were measured under the xenon-arc lamp of an Opti-Beam 1000 solar simulator producing the AM 1.5 spectrum.

From the work cited above we already knew that Cl reduces the conductivity of undoped *a*-Si:H films (from 1×10^{-11} to $1 \times 10^{12}\text{ S/cm}$ in our case). This observation supports the view that Cl is a weak *p*-type dopant in *a*-Si:H,³ and true confirmation comes from thermoelectric power measurements.⁴ Our dark conductivity measurements show that chlorine reduces the dark conductivity of phosphorus-doped *a*-Si:H films from 2×10^{-3} to $8 \times 10^{-6}\text{ S/cm}$ (for the dc case) or 4×10^{-3} to $7 \times 10^{-5}\text{ S/cm}$ (for the rf case). This confirms a previous result for such films deposited from H_2 and SiCl_4 .⁵ Other groups depositing from dichlorosilane did not observe this effect, probably because their gas phase concentration of PH_3 was significantly higher than ours, and because their films are microcrystalline rather than amorphous.^{4,6} We hypothesize that in the solar cells described above, when the Cl in the *i* layer comes in contact

^{a)}Author to whom correspondence should be addressed; electronic mail: ampayne@ee.princeton.edu

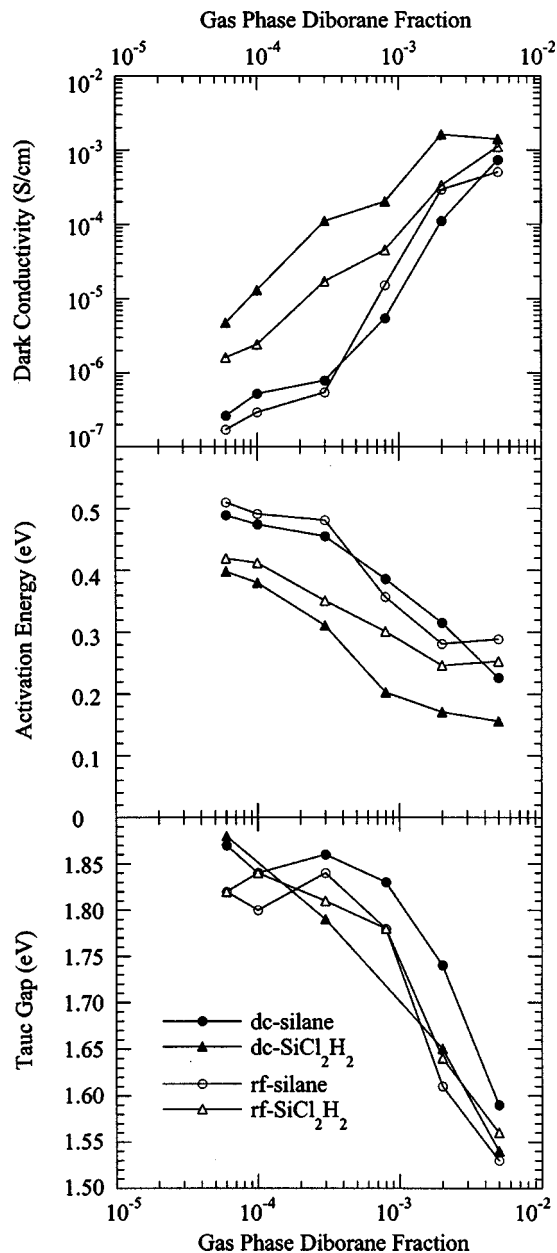


FIG. 1. Room temperature dark conductivity, activation energy, and Tauc gap as a function of gas phase diborane fraction.

with the n layer, the presence of the Cl at the i/n interface reduces the neutral portion of the n layer by reducing the conductivity and thus decreases V_{oc} . In contrast to the P-doped and undoped films, the B-doped films showed a significant increase in conductivity.

The optical and electronic properties of the films are shown in Fig. 1. From this figure we see that the chlorinated films have higher conductivity except at the highest gas phase concentration of diborane, where the conductivities are the same. We also note that the conductivity enhancement with Cl is more noticeable for the dc deposited films. The activation energies of these films support the observation that the conduction comes from holes via thermal activation, and not through a change in the conductivity prefactor, again, except for the highest concentrations of boron. Although these films show a decrease in Tauc gap with increasing boron concentration, the optical properties are not changed in any systematic way by the addition of chlorine. The decrease

TABLE I. Impurity concentrations (in 10^{19} cm^{-3}) of various films as measured by SIMS.

Film ^a	[H]	[O]	[C]	[Cl]	[B]
$p\text{-SiH}_4$, 6×10^{-5}	200	b	b	b	4.6
$p\text{-SiH}_4$, 30×10^{-5}	200	b	b	0.004	17.0
$p\text{-SiH}_4$, 80×10^{-5}	200	b	0.20	0.020	31.0
$p\text{-SiCl}_2\text{H}_2$, 6×10^{-5}	200	3.0	0.20	30.0	5.8
$p\text{-SiCl}_2\text{H}_2$, 30×10^{-5}	250	2.5	0.20	30.0	22.0
$p\text{-SiCl}_2\text{H}_2$, 80×10^{-5}	250	2.0	0.30	40.0	41.0
$i\text{-SiH}_4$	200	b	b	b	b
$i\text{-SiCl}_2\text{H}_2$	200	2.0	0.30	20.0	b
$n\text{-SiH}_4$	300	b	b	b	b
$n\text{-SiCl}_2\text{H}_2$	200	2.0	0.10	20.0	b
$p\text{-SiH}_4$, 30×10^{-5} rf	300	b	b	0.005	18.0
$p\text{-SiCl}_2\text{H}_2$, 30×10^{-5} rf	200	b	b	20.0	16.0
Background	—	1.0	0.04	0.002	0.01

^aThe boron-doped (p -type) samples are designated by the gas fraction of B_2H_6 .

^bIndicates a concentration equal to the detection limit of SIMS (listed in the last row).

in Tauc gap at the highest boron incorporation rates has been observed previously and is related to the structural changes as boron alloys of $a\text{-Si:H}$ are formed, but is unrelated to the chlorine content of the films.⁷ These structural changes also alter the conductivity prefactor. We therefore rule out increased boron incorporation as an explanation for the increased conductivity. Secondary ion mass spectroscopy (SIMS) was performed at Evans East for confirmation of the actual solid phase concentration of boron in the films, which could differ from the gas phase concentration of the dopant-bearing gas. The results are shown in Table I. The first observation is that the gas fraction of diborane does correlate well with the solid phase concentration of boron, as expected from the standard doping model.¹ The second observation is that boron incorporation is enhanced by approximately 30% by Cl for the dc deposited films, but is reduced by 10% for the two B-doped rf films measured in this fashion. A 10%–30% change in boron concentration should cause only a corresponding 10%–30% change in conductivity, which would be beneath the limits of our conductivity measurement to distinguish, and cannot account for the order of magnitude difference actually measured for these films. Because the concentration of chlorine is roughly the same for all concentrations of boron (Table I), chlorine by itself cannot account for the conductivity increase. Therefore, we conclude that chlorine *enhances the doping efficiency of boron* in $a\text{-Si:H}$.

It is known that hydrogen passivates boron in B-doped crystalline silicon.⁸ Recent calculations⁹ indicate that a simi-

TABLE II. Room temperature dark conductivity, activation energy, and Tauc gap for the $a\text{-SiC:H}$ films.

Film	α_{dark} (S/cm)	E_{act} (meV)	E_{Tauc} (eV)
$p\text{-SiC:H}$	1.2×10^{-5}	366	1.87
$p\text{-SiC:H,Cl}$	1.4×10^{-4}	290	1.80
$i\text{-SiC:H}^a$	7.5×10^{-13}	967	1.90
$i\text{-SiC:H,Cl}^a$	6.4×10^{-14}	984	1.90

^aBecause the room temperature dark conductivity of the intrinsic $a\text{-SiC:H}$ films was beneath the noise level of our measurement apparatus, these conductivity numbers were extrapolated from higher temperature measurements.

TABLE III. Solar cell characteristic parameters for cells incorporating chlorinated and unchlorinated p layers of a -SiC:H of differing thicknesses.

Cell, Thicknesses	Eff. (%)	FF	V_{oc} (V)	J_{sc} (mA/cm ²)
Standard, 13 nm	6.87±0.1	0.66±0.01	0.76±.01	13.72±0.1
Cl, 13 nm	7.53±0.2	0.66±0.01	0.76±.01	14.96±0.1
Standard, 16 nm	6.86±0.1	0.66±0.01	0.75±.01	13.83±0.1
Cl, 16 nm	6.91±0.1	0.65±0.02	0.76±.01	13.99±0.1
Standard, 26 nm ^a	5.99	0.62	0.79	12.20
Cl, 26 nm	5.99±0.2	0.61±0.03	0.73±.02	13.11±0.1

^aProcessing problems precluded the fabrication of multiple devices for this cell, so that statistical errors could not be calculated.

lar effect is responsible for the low doping efficiency of boron in a -Si:H. Boron and chlorine may form a cluster which is an acceptor site that is not affected by the passivating presence of nearby hydrogen.

Intrinsic and p -type a -SiC:H films were also deposited and their dark conductivity and Tauc gaps are listed in Table II. In the intrinsic films the Tauc gap is not altered by Cl, but in the boron-doped films the Tauc gap is decreased by 0.07–0.08 eV, which accounts for the difference in conductivity. Table III shows the solar cell current–voltage characteristics for cells utilizing the boron-doped a -SiC:H, Cl layers as their p layer. Because the activation energy of the chlorinated p -Si:CH, Cl is lower than the unchlorinated alloy, we expect the splitting of the quasi-Fermi levels to be greater, and therefore produce a larger open circuit voltage. However, the open circuit voltages of these cells are the same, to within experimental error. The efficiency increase occurs because of a rise in the short circuit current density. Because there was no increase in open circuit voltage, some factor other than the doped layer activation energy is limiting it, such as charged defects in the i layer. Nevertheless, chlorinated a -SiC:H p layers present one method for increasing the efficiency of a -Si:H based solar cells.

In conclusion we note that the conductivity in B-doped a -Si:H, Cl is enhanced over B-doped a -Si:H. This increase occurs from a gas phase dopant range of 60 ppmv to 0.5 vol % for both dc and rf plasma excitation. The conductivity increase is also observed for a -SiC:H, albeit there it is coupled with a reduction in the Tauc gap. Band gap changes and enhanced incorporation of boron were ruled out as causes for this effect in a -Si:H. An acceptor cluster of B–Cl not passivated by nearby H is proposed as the possible origin of the enhanced conductivity. Solar cells were fabricated utilizing chlorinated a -SiC:H p layers. The solar cells showed improved efficiency, but no enhanced open circuit voltage.

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