Observation of a Reversible Field-Induced Doping Effect in Hydrogenated Amorphous Silicon

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The observation of a metastable field-induced doping effect which occurs in the bulk of n-type hydrogenated amorphous silicon films at temperatures above 150 °C is reported. This effect produces a reversible tenfold change in the net shallow donor concentration and thus is intimately related to the overall doping mechanism of these films.

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Metastable effects in hydrogenated amorphous silicon (a-Si:H) have recently attracted great interest. The most widely studied has been the light-induced conductivity change discovered by Staebler and Wronski.[1] Another effect is the apparent change in conductivity induced by applying an electric field of $(1-5)\times 10^4$ V/cm to the sample at temperatures above about 150 °C.[2-4] However, Solomon, Dietl, and Kaplan[2] have argued quite convincingly that this latter effect is most likely due to the motion of ionic charge in the substrate and hence is a spurious phenomonon not related to the true bulk properties of a-Si:H. In this Letter we show that there is in fact a field-induced doping effect which is clearly a bulk property of a-Si:H. We see a dramatic increase in the net shallow donor concentration by a factor of 10 which is generated by high electric fields ($\gtrsim 10^5$ V/cm) at temperatures above 150 °C. The effect produces a metastable state at room temperature and is completely reversible. The proposed models for this phenomenon shed light on the broader question of the overall doping mechanism in a-Si:H.

The experimental technique which we have used involves the measurement of thermally induced reversible changes in the capacitance of Schottky barrier structures fabricated on thin films (~ 1–2 μm) of n type a-Si:H. The a-Si:H films were grown by rf decomposition of silane at 250 °C as described elsewhere.[5,6] Most of the films were lightly doped with PH_3 (100–1000 ppm PH_3/SiH_4), but a few were unintentionally doped, apparently by a leak or impurity in the growth system.[5,6] In all cases the film conductivity was high enough that the bulk dielectric relaxation time was fast compared to the capacitance measurement frequency (0.1–1.0 MHz). Thus the capacitance measurements reflect the properties of the series combination of two space-charge layers; one at the Schottky barrier on the surface ("front junction") and the other at the interface with the heavily doped crystalline silicon substrate ("rear junction"). Such back-to-back junction structures are straightforward to analyze for bias voltages greater than a few tenths of a volt and their capacitances are dominated by the properties of the reverse-biased member of the junction pair.[6] Therefore, by changing the polarity and magnitude of the applied bias one may probe both the front and rear sides of the a-Si:H film to depths of a few tenths of a micron.

The most straightforward means of seeing the field-induced doping effect is in the capacitance-voltage (C-V) curve measured at 300 K following a 10 min anneal at 200 °C with an applied bias voltage. Results of several such anneals are shown in Fig. 1. The major effect is to shift the C-V curve of the affected junction along the voltage axis by an amount nearly equal to the bias

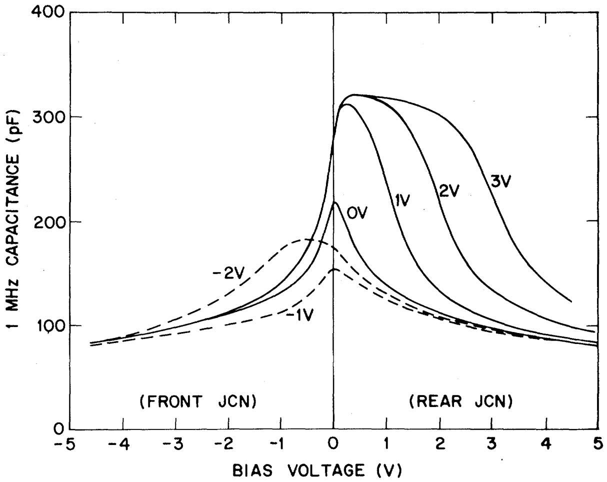

FIG. 1. Capacitance vs bias voltage (C-V) curves recorded at 300 K for a series of different annealing conditions. The voltage labels correspond to the bias applied during 10-min anneals at 200 °C.

voltage during the anneal. This C-V shift occurs for both polarities of the annealing voltage, i.e., for both the front and rear junctions, and can be returned to a state close to the original C-V curve by annealing at 200 °C with zero bias for 10 min. After this small hysteresis in the initial cycle to the field-induced state and back to the zero-field state, further cycling is completely reversible. The zero-field state in Figs. 1 and 2 corresponds to the condition after several such cycles.

The fact that the C-V shift is due to a bulk doping change is most apparent from the *derivative* of the C-V data. This is most conveniently presented as the C-V doping profile $N_{CV}(x) = -(C^3/\epsilon q A^2)(dC/dV)^{-1}$, where C, ϵ, and A are the capacitance, dielectric constant, and area, respectively, of the diode, q is the electronic charge, V is the applied bias, and $x = \epsilon A/C$ is the width of the depletion layer in the high-frequency limit.[6,7] Such a profile is shown in Fig. 2 for a lightly doped sample in which the front junction (Schottky barrier) depletion depth in the zero-field state was adjusted from less than 0.2 μm to greater than 1.0 μm by varying the bias from 0 to -20 V. The field-induced doping effect is manifested in this figure by the tenfold increase in N_{CV} within the depletion region which was present at the anneal bias. The slight undulations in N_{CV} versus x in Fig. 2 are due to real spatial variations in the doping concentration incorporated during film growth. Note that these undulations are at the same values of x for the various anneal conditions even though the C-V bias voltage for corresponding features changed considerably with annealing. This is strong evidence that the field-induced doping effect in Fig. 2 is a *bulk* property of the material.

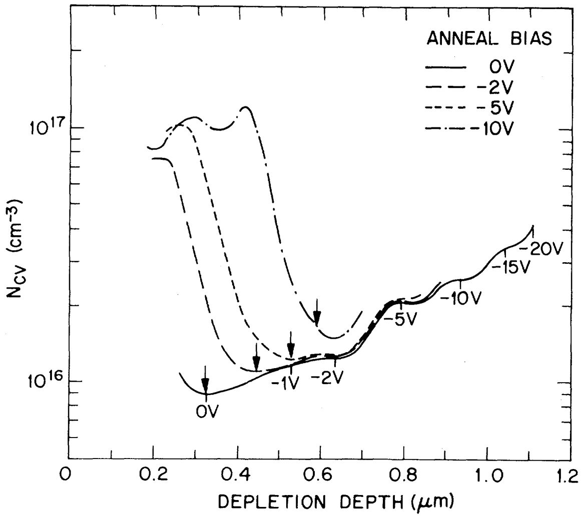

FIG. 2. C-V doping profile measured at 300 K following four different bias anneals (0, -2, -5, -10 V). The arrows indicate the depletion width for a measurement bias equal to the anneal bias in each case; the tic marks indicate the bias dependence of the depletion depth for the $V = 0$ case (zero-field state).

The quantity N_{CV} is a convenient measure of the net doping of the sample, but its precise meaning in terms of the density of gap states in a-Si:H is somewhat complex.[6,8] In our case we have used a special ac method[7] of measuring dC/dV so that N_{CV} may be directly interpreted as the net shallow donor concentration (more precisely, the integral of band tail states from $E_C - 0.5$ eV up to the Fermi level).[6,8] Thus the field-induced increase in N_{CV} in Fig. 2 is a true doping effect and not the trivial result of deep traps or ionic charge at the substrate interface. The effect was seen in all of the conducting samples examined; N_{CV} in the zero-field state (state A of the Staebler-Wronski effect[1]) ranged from less than 10^{16} cm^{-3} to greater than 10^{17} cm^{-3} in the various samples. In all cases the field-induced doping effect increases N_{CV} by approximately an order of magnitude.

The temperature dependence of the reversible annealing rate was obtained by observing the capacitance transient which results after a step-function change in the bias at temperatures in the range of 140 to 200 °C. The actual time dependence is nonexponential and must be observed on a logarithmic time scale over at least four decades. The maximum slope of C versus $\ln t$ is found to occur at the half signal point, and we have taken this as the characteristic annealing time. The annealing rate is the same both into and out of the enhanced doping state and is equal to $(6.4\times 10^7\ \mathrm{sec}^{-1})\exp(-0.87eV/kT)$. Note that this is very close to the annealing rate seen by Ast and Brodsky[3] in their conductivity experiments. Thus, while extraneous interface effects[2] cannot be ruled out for such measurements, it is likely that they were actually seeing the bulk doping effect reported here.

The detailed mechanism for this doping change is obviously quite complex. However, some comments are in order to shed light on both this particular effect and the overall doping mechanism in general. First, we note that while we have referred to this effect as induced by the electric field of the barrier depletion layer, we do not know whether the doping effect is *directly* related to the field or *indirectly* related via the changed Fermi level in the depletion layer. We do know, however, that the effect is *not* a simple trapped-electron emission process which is commonly observed in juction depletion layers.[5,6,8] This is clear from the very small ($< 10^8$ sec^{-1}) prefactor of the annealing rate. Detrapping processes typically have prefactors on the order of an atomic vibrational frequency of 10^{12} sec^{-1} and have never been measured to be less than 5×10^{10} sec^{-1}. Nevertheless, the field-induced doping effect does give rise to a thermally activated capacitance transient which could at first be mistaken for a trapping effect when observed by deep-level transient spectroscopy.[9] The observed reduction of the prefactor by four orders of magnitude indicates a more involved thermal process, e.g., long-range diffusion over a distance of $(10^4)^{1/2}\times 3$ Å, or a reaction with a second species of fractional concentration 10^{-4}, or a thermally assisted tunneling process.

We should like to mention two general mechanisms which are both consistent with our observations. First, the field-induced doping effect is consistent with the autocompensation mechanism proposed by Biegelsen, Street, and Knights[10] to explain the dependence of the doping-induced defect density on the position of the Fermi level during film growth. In Fig. 2 the larger steady-state doping occurs within the junction depletion layer where the quasi Fermi level is depressed by the electric field to midgap from its equilibrium position ($0.15 < E_C - E_F < 0.3$ eV in our various samples).[6] This is precisely what would be expected from the model of Biegelsen, Street, and Knights[10] if the defect reactions which they proposed can be induced in the film after growth.

A second mechanism is suggested by the quantitative results which have been obtained concerning *a*-Si:H doping mechanisms. We typically find in our films that N_{CV} in the zero-field state is about 10^{-2} of the PH_3/SiH_4 ratio in the plasma. Knights, Hayes, and Mikkelsen[11] and Thomas[12] have shown that in their typical films the concentration of donor impurities in the solid is within a factor of 2 of the gas-phase ratio. The extended x-ray absorption fine structure measurements of Knights, Hayes, and Mikkelsen[11] indicate that 0.2 ± 0.1 of the dopant impurities are fourfold coordinated. If these results also apply to our films, then N_{CV} in the zero-field state is an order of magnitude lower than the expected concentration of fourfold coordinated atoms. Since the field-induced doping effect increases N_{CV} by an order of magnitude, it is tempting to think that this represents activation of the full concentration of fourfold coordinated donors indicated by the extended x-ray absorption fine structure results. It may be that most of the potential fourfold-coordinated donors are in some way compensated by hydrogen or some efect in the zero-field state and are activated by the high-field anneal. The activation of donors may then take place by field-assisted diffusion of H (or P?) atoms over distances of order of 300 Å, which is also of order of the columnar diameter in these thin films.[13] The P atoms may be segregated at the columnar interfaces, as suggested by Phillips through scaling and chemical bonding arguments.[14] If the columnar surfaces primarily have local (111) texture, then the average spacing of edges with (100) texture[14] will also be 300 Å, so that the activation mechanism could consist of surface diffusion from the former to the latter sites. The observed low activation energy (0.87 eV) is *only* consistent with surface or grain boundary diffusion. This mechanism is also consistent with the recent concentration profile work of Toulemonde *et al.*[15] showing a tendency of H to be spatially associated with the donor concentration.

In summary, we have reported the observation in *a*-Si:H of a reversible doping enhancement effect which occurs in the high-field region of a junction space-charge layer at temperatures above 150 °C. We show that this field-induced doping is a bulk effect and discuss various models which relate it to possible doping mechanisms in *a*-Si:H.

We are indebted to J. C. Phillips for pointing out to us the topological significance of the anomalously small prefactor of the annealing rate.

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Transient-Capacitance Measurement of the Grain Boundary Levels in Semiconductors

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The transient response of a grain boundary to a voltage pulse is discussed in terms of the basic capture and emission processes at the boundary states. This model is used to interpret the deep-level transient spectroscopy spectrum of a low-angle tilt boundary with a known dislocation structure in a germanium bicrystal. A characteristic level is found at 0.42 eV below the bottom of the conduction band; the number of states at this level is about 10^9 cm^{-2} and their capture cross section for electrons is 5×10^{-12} cm^2.

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With few exceptions,[1-3] the electrical properties of grain boundaries in semiconductors have been investigated from steady-state measurements only: The barrier height is determined from the capacitance and from the current-voltage characteristics,[4,5] and the grain-boundary density of states can then be derived by an appropriate deconvolution scheme.[6] However, both the density of states and the capture cross sections can be obtained more directly from the transient response, after voltage pulses have been applied across the boundary.[3,7] In this Letter we first give a description of the transient response in the model generally accepted for a grain boundary.[4] We then describe the experimental results obtained in the case of a low-angle tilt boundary in a germanium bicrystal.

Figure 1(a) shows the well-known energy band structure at a grain boundary in n-type material.[4] As discussed in a previous paper,[8] at low enough temperatures the boundary charge is screened by the ionized impurities in the depleted regions on both sides of the boundary. Changes in the occupancy of the boundary levels can be detected from the concomitant changes in the grain boundary capacitance. Provided the hole contribution can be neglected, the conduction electrons are solely involved in the capture and emission processes at the boundary states. If we consider the latter as a discrete set of levels (which will be justified below), the emission rate from a level at energy E_0 is given by[9]

$$e_n = 2N_c\sigma\bar{v}_{\text{th}}\exp[-(E_c-E_0)/kT], \qquad (1)$$

where σ is the capture cross section of the boundary level, N_c is the effective number of states in