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Improved material properties of amorphous silicon from silane by fluorine implantation: Application to thin-film transistors

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In this paper it is reported for the first time that the material properties of hydrogenated amorphous-silicon films deposited from a pure silane plasma can be improved by a low-dose fluorine implantation. It is shown that the field-effect density of states is reduced after implantation and appropriate annealing. The implanted material shows a better photostability as well as a better resistance against prolonged electric field application and against exposure to temperatures above deposition temperature.

I. INTRODUCTION

Amorphous-silicon alloys receive considerable interest because thin films of these alloys can be prepared easily over large areas for application, among others, in photovoltaic modules and in liquid crystal display (LCD) panels. Thin-film transistors (TFTs) made of hydrogenated amorphous silicon (*a*-Si:H) are currently used in prototypes as well as in commercially available LCDs.[1]

The amorphous material combines the advantages of a capability for large area technology and a modifiable energy band gap along with semiconducting properties of single-crystal silicon such as dopability and compatibility with dielectrics. A major drawback of amorphous silicon is, however, its inherent instability, which has found expression in, for instance, photostimulated creation of dangling bonds (the Staebler–Wronski effect[2,3]), and the field-induced creation of interface states in semiconductor/insulator structures.[4,5] As stability is becoming a key issue in many applications, it is not just of academic interest to investigate the origin of degradation effects and the possibilities to either avoid or eliminate these effects. Feasible approaches include adjusting the material by alternative production techniques[6] or technologically bypassing the problem under device operating conditions.[7] A more elegant solution is to produce inherently stable materials.

Early publications[8,9] on fluorinated amorphous-silicon films deposited from SiF_4/H_2 mixtures reported that these films showed no photostructural changes and that they were in more respects superior to silane-based films. Also silicon-germanium alloys have been reported to show a lower density of gap states and an improved photoresponse by using fluorine-containing gases during deposition.[10] It has been pointed out by Guha[11] that the presence of F reduces light-induced effects in these alloys. In the first instance one would expect that fluorine, being a stronger electronegative agent, has the role of saturating germanium dangling bonds. However, since the fluorine concentration in these alloys, similar to *a*-Si:H, is very small (0.1%–6%,[9,11,12]), it is questionable whether the beneficial effects are due to the fluorine actually bonded in the film or to the presence of fluorine-containing species in the glow discharge.

The purpose of this report is to address the above question and to present the results on post-deposition low-dose implantation of fluorine in *a*-Si:H films deposited from silane only. There are only a few publications on hydrogenation or fluorination of amorphous silicon by implantation,[13–18] presenting a variety of results.

Kalbitzer *et al.*[13] used implantation of halogens in *a*-Si:H, but they found an increase in the density of gap states as observed by photoconductivity measurements. They do not discuss the stability of the implanted material.

Most publications report on implantation into material with an initially high density of defects on the order of 10^{18}–10^{19} cm^{-3}. Neudeck and Lee[14] successfully applied H implantation in vacuum-evaporated *a*-Si, thus reducing the density of gap states by about two orders of magnitude. Suzuki, Hirose, and Osaka[15] have observed a similar decrease in the density of gap states by implantation of H into chemically vapor deposited (CVD) *a*-Si, followed by annealing at 300 °C. The as-desposited film, however, had an initial electron spin resonance (ESR) defect density as high as 10^{19} cm^{-3}. Tsuo, Smith, and Deb[16] reported on ion beam hydrogenation of deliberately dehydrogenated amorphous silicon. They found that the implanted hydrogen is predominantly bonded as Si—H and they observed a lack of light-induced degradation in both photo- and dark conductivity.

Janai *et al.*[17] employed implantation of additional F in *a*-Si:F deposited from SiF_2 and found an increase in dc conductivity which was attributed to implantation damage. Apparently, they used a too high implantation dose and energy (2×10^{16} cm^{-2} at 90 keV).

Ishikawa and Wilson[18] found that although implantation of H and F into evaporated *a*-Si films did not result in a material quality equal to plasma-deposited *a*-Si:H, the density of gap states could be reduced substantially. They report the existence of an optimum F dose, which appears to be higher than the optimum dose reported in this paper. This is probably due to the difference in starting material.

The present report is, in contrast to the above-mentioned papers, concerned with the implantation of F into a conventional plasma-deposited device-quality hydrogenated amorphous silicon film.

The implantation technique is widely used in crystalline semiconductor technology and could also become useful in the amorphous-silicon field. It has the advantage of permit-

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ting independent control of amorphous-silicon composition and dopant concentration. On the other hand, it is known to create point defects and voids by the bombardment of energetic ions. It has even been suggested[19] that the implantation technique cannot be successful, because annealing would not permit the local order rearrangements necessary to remove the point defects and voids created by the bombardment. Other publications,[20,21] however, have demonstrated that defects created by a low-dose implantation with chemically inert ions can be removed completely by a short low-temperature anneal. This is due to the facility of hydrogen motion and the inherent flexibility of the amorphous network.

The study of electronic and optical characteristics was performed in a thin-film transistor. Being a planar device, the implantation technique is of particular interest to the thin-film transistor. In the following we will characterize the F-implanted films by the field-effect density of states and the generation efficiency (η)-electron mobility (μ)-electron lifetime (τ) product. We will discuss the degradation as caused by field stressing, intense illumination and heat treatment.

II. EXPERIMENTAL DETAILS

The substrates used are highly doped ($\rho = 1$–15 mΩ cm) n-type single-crystal (100) silicon wafers. A silicon dioxide layer of 110 nm thickness was thermally grown in dry oxygen at 1000 °C to serve as the gate insulator. Five a-Si:H films of thickness 430 nm, hereafter labeled A through E, were simultaneously deposited by rf glow-discharge decomposition of silane (SiH_4) at a substrate temperature of 250 °C. The rf power density and pressure were maintained at 30 mW/cm^2 and 0.4 Torr, respectively.

Then, four samples were implanted with F^+ ions using a 200-kV Extrion implanter. The implantation was done at a low dose and a low energy (25 keV) in order to prevent implantation damage in the conducting channel region. The implant doses were 1×10^{14}, 5×10^{14}, 1×10^{15}, and 5×10^{15} cm^{-2} for samples A–D, respectively, corresponding to a volume density between 2×10^{18} and 1×10^{20} cm^{-3}, whereas sample E was not implanted. To eliminate implantation damage all specimens, including the unimplanted reference, were annealed in N_2 at 210 °C for 1 h.

A passivating SiO_x layer of thickness 150 nm was plasma deposited at 250 °C in a gas mixture of SiH_4 and N_2O at a flow ratio of 15 to 85. In this layer contact holes were etched to define the geometry of source and drain contacts. Then, P^+ ions were implanted (30 keV, 1×10^{16} cm^{-2}) in all five samples to produce a thin n^+ a-Si:H layer. Aluminum was e-gun evaporated and patterned by photolithography. A post-metallization anneal of 30 min at 200 °C was necessary for the formation of ohmic contacts.[22] The complete structure is shown in Fig. 1.

Field-effect characteristics (transfer characteristics) were measured by stepwise variation of the gate voltage V_g at a drain voltage V_{ds} of 0.25 V. To determine the ohmicity of the contacts, output characteristics (drain current I_{ds} versus drain voltage V_{ds}) were measured at conducting channel conditions ($V_g = 10$ V).

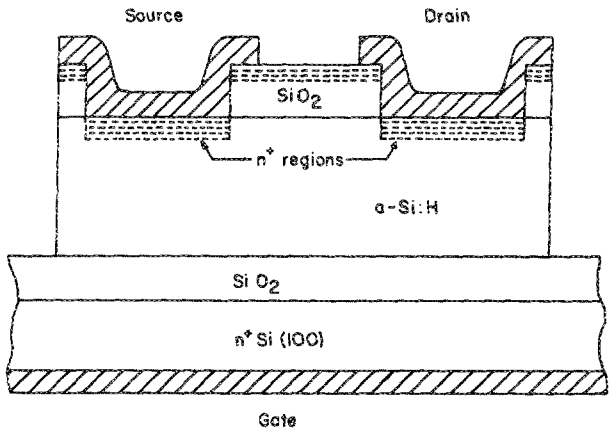


FIG. 1. Cross section of the amorphous-silicon staggered electrode thin-film transistor.

To investigate the effect of intense illumination (Staebler–Wronski effect), the TFTs were illuminated with white light originating from a 150-W tungsten light source, appropriately heat filtered such that the TFTs were exposed to an intensity of 200 mW/cm^2 of visible light only (350–700 nm). The transfer characteristics were measured before and after 3 h of continuous illumination. The photocurrent was monitored during illumination. The spectral sensitivity of the photocurrent has been obtained by using monochromatic photon fluxes F_0 of 10^{12}–10^{13} photons/cm^2 s at photon energies from 1.7 to 2.7 eV and was measured before and after the exposure period. Here, the field-effect structure, in contrast to conventional gap electrode configurations, offers the ability to establish a well-known band-bending situation. In this way apparent changes due to charging and discharging of the interface are avoided.[23,24] It was confirmed that the light-induced changes were reversible by annealing the structures in air at 170 °C.

The degradation due to field-induced interface states was studied by recording the field-effect current for 2.3×10^5 s at a drain voltage of 0.25 V and a temperature of 65 °C during continuous application of a gate voltage of + 10 V, which corresponds to a transverse field of 3×10^5 V/cm.

The heat-resistance of the amorphous material was test-

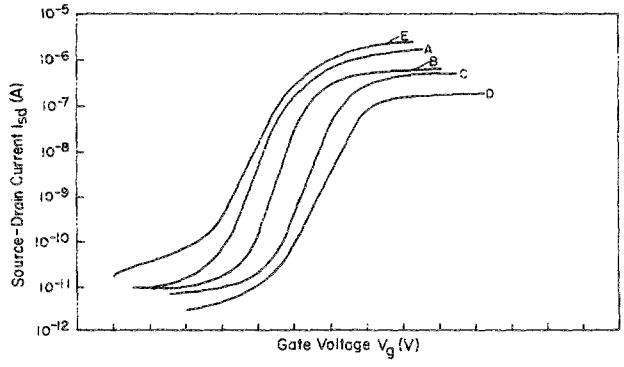


FIG. 2. Transfer characteristics for F-implanted TFT structures. Implant dose for (A) 1×10^{14} cm^{-2}, (B) 5×10^{14} cm^{-2}, (C) 1×10^{15} cm^{-2}, (D) 5×10^{15} cm^{-2}, (E) was not implanted. For clarity successive characteristics have been displaced by 0.5 V along the V_g axis. For all devices the gate voltage was varied from − 2 to 6 V. The drain voltage was 0.25 V.

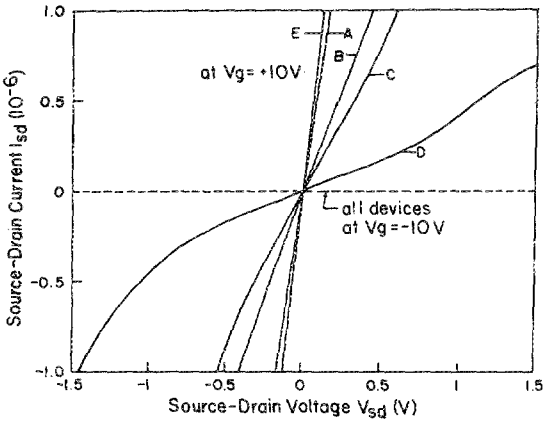


FIG. 3. Measured output characteristics of the same F-implanted devices as in Fig. 2. The gate voltages used are − 10 and + 10 V.

ed by determining the change in channel conductivity at 65 °C, due to a heat treatment at 300 °C for 20 min in a dry N_2 ambience. It was assured that contacts did not deteriorate due to this treatment.

III. RESULTS

A. Density of states

In Fig. 2, transfer characteristics are shown for all five TFT structures. It is seen that there is an optimum in the slope of I_{ds} vs V_g in the prethreshold region. The current capability at $V_g = +10$ V decreases monotonously with F content. This is due to the influence of the source and drain contacts, as is seen in Fig. 3, where it appears that the series resistance increases with increasing F implantation dose.

A rough number for the density of gap states N_F was obtained from the logarithmic slope of the I_{ds}-V_g curve, using the method of Neudeck and Malhotra.[25] The density of gap states N_F is essentially calculated from

$$N_F = \frac{\epsilon_0}{\kappa_{si}} \left(\frac{\kappa_{ins}}{k_B T d_{ins}} \frac{dV_g}{d(\ln I_{ds})} \right), \qquad (1)$$

where ϵ_0 is the permittivity of free space, κ_{si} is the relative dielectric constant of amorphous silicon ($\kappa_{si} = 11.8$), κ_{ins} is the dielectric constant of the gate insulator ($\kappa_{ins} = 3.85$), k_B is Boltzmann's constant, T is the measurement temperature,

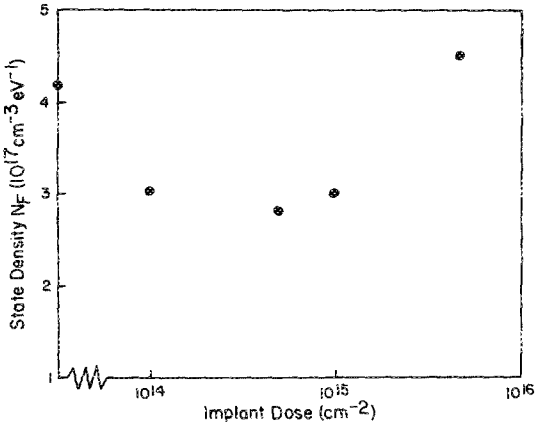
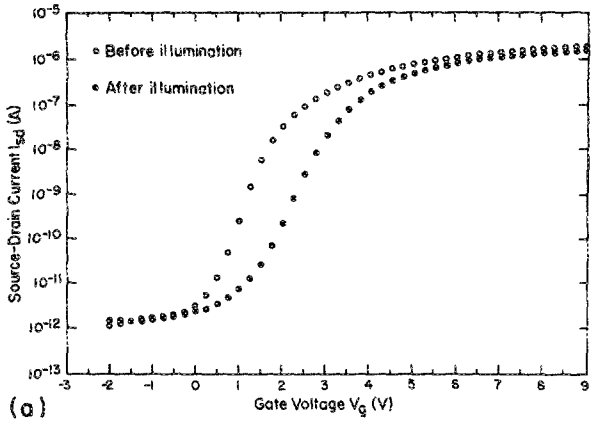


FIG. 4. The density of gap states N_F determined by the field-effect technique as a function of implantation dose.



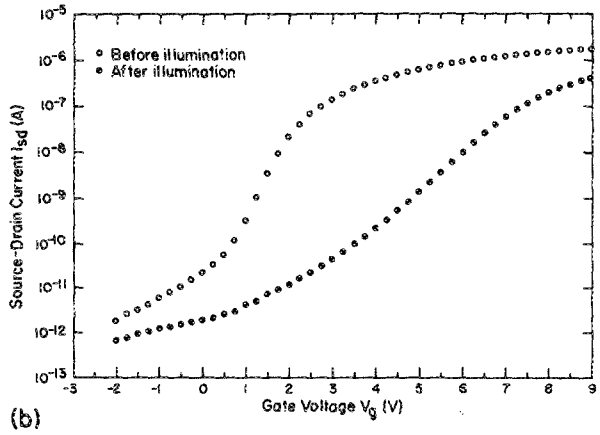


FIG. 5. Transfer characteristics before (○) and after (●) visible light (350–700 nm) illumination at an irradiance of 200 mW/cm² for a period of 3 h; (a) measured in a lightly flourinated device; and (b) measured in an unfluorinated device with the a-Si:H layer deposited in the same run.

d_{ins} is the thickness of the gate insulator, and $dV_g/d(\ln I_{ds})$ is the slope in the subthreshold region of the field-effect curve. In Fig. 4, the value for N_F is shown for all five implantation doses.

B. Photoinduced degradation

Figures 5(a) and 5(b) show transfer characteristics before and after light soaking of a low-dose fluorine-implanted and an unimplanted TFT. It is clearly seen that light soaking causes a threshold voltage shift accompanied by a decrease in the subthreshold slope. Both changes are much less pronounced in the fluorinated device. The densities of gap states calculated from the subthreshold slopes, using Eq. (1), are listed in Table I.

Figure 6 shows the normalized photocurrent as a function of exposure time. If we express the magnitude of the Staebler–Wronski effect by $\sigma_{phB}/\sigma_{phA}$, where σ_{phB} and σ_{phA}

TABLE I. Density of states (cm^{-3} eV^{-1}) in the initial state and after light exposure.

	Unimplanted specimen	F-implanted specimen
Initial state	4.2×10^{17}	3.1×10^{17}
After exposure	3.4×10^{18}	5.3×10^{17}

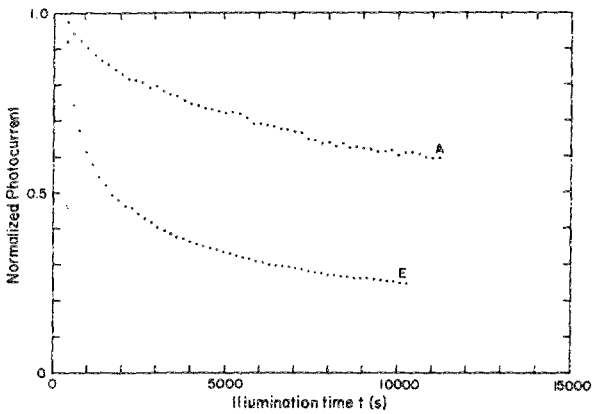


FIG. 6. Decrease in the photocurrent as a function of exposure time during exposure to visible light at 200 mW/cm^2.

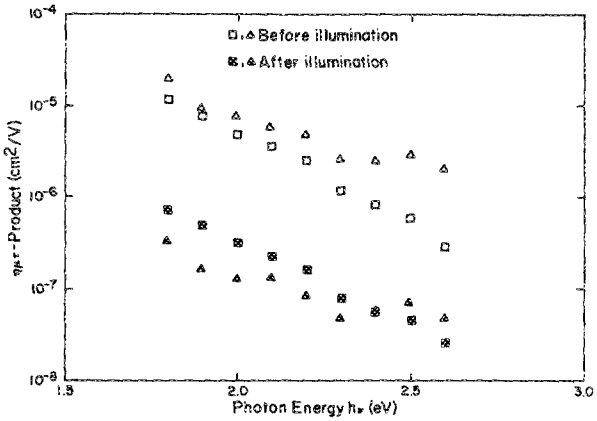


FIG. 7. Measured quantum efficiency-mobility-lifetime ($\eta\mu\tau$) products as a function of photon energy for a fluorine-implanted sample, before (□) and after (■) illumination, and for an unimplanted sample, before (△) and after (▲) illumination. $V_{sd} = 0.25$ V, $V_g = V_{FB}$.

refer to the photoconductivity just after and before 3 h of illumination at 200 mW/cm^2, we obtain $\sigma_{phB}/\sigma_{phA} = 0.59$ for the fluorinated and 0.24 for the unfluorinated sample.

In order to assure true bulk transport of majority carriers uninfluenced by accumulation layers at the insulator interface, spectral sensitivity measurements were carried out at flat bands or slightly upward bands ($V_g \lesssim V_{FB}$). As has been shown in an earlier report[22] and as observed in Figs. 1 and 2, hole transport is effectively blocked under these conditions so that secondary photocurrent measured is due to electrons only.

For a rough approximation of the generation efficiency (η)-electron mobility (μ)-electron lifetime (τ) product, we used the relation[26]

$$I_{ph} = eF_0(1-R)[1-\exp(-\alpha d_{si})]\eta\mu\tau(W/L)V_{ds}, \quad (2)$$

where I_{ph} is the measured photocurrent, e is the electronic charge, R is the reflection from the surface, α is the absorption coefficient of amorphous silicon, d_{si} is the thickness of the amorphous silicon layer, V_{ds} is the drain-source voltage, W is the channel width, and L is the channel length. The absorption coefficient was determined from reflection and transmission measurements on a-Si:H films prepared under the same conditions on quartz substrates. It was assumed that the implantation did not change the optical properties.

In Fig. 7 it is observed that the fluorinated amorphous-silicon film, though exhibiting a lower initial value for $\eta\mu\tau$, possesses a higher stability than the unfluorinated film, such that the final values for $\eta\mu\tau$ actually end up larger.

Upon checking the reversibility of the degradation effects, the interesting effect was observed that fluorinated samples require a longer anneal time than the nonfluorinated samples in order to return to their initial state. The photoconductivity was restored after 3 h at 170 °C in a nonfluorinated device, whereas it took approximately 9 h for a fluorinated device.

C. Field-induced effects

As is commonly observed in a-Si:H TFTs, a continuous application of a gate bias produces a threshold voltage shift in the transfer characteristics. Figure 7 displays the decay of the ON-current, due to continuous application of a fixed gate voltage. Although the initial currents are lower in the samples with F, the absolute final currents are higher than in the sample without F. This is demonstrated in Fig. 8.

D. Heat resistance

It is generally observed that the electronic properties of a-Si:H deteriorate if the material is annealed above the deposition temperature. This restricts the maximum tolerable temperature in the processing of devices and could, in principle, cause slow degradation of the material at operating temperatures. In order to investigate the temperature stability of our TFTs, the completed structures were annealed at 300 °C in a dry N_2 ambience for 20 min. Both samples with and without F showed a decrease in the ON-current measured at $V_g = 10$ V, $V_{sd} = 0.25$ V, and $T = 65$ °C, but the final current in the fluorinated TFT is higher than in the nonfluorin-

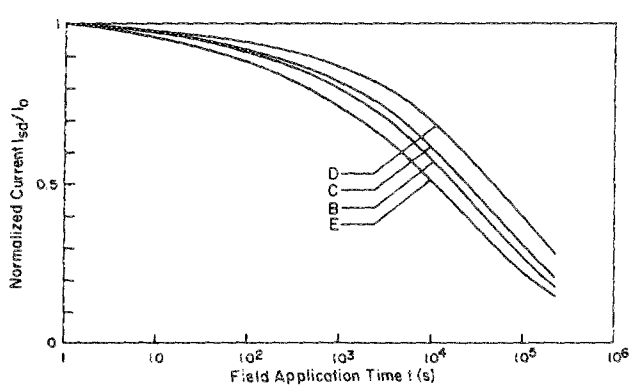


FIG. 8. Decrease in the ON-current vs time of a series of TFTs differently implanted with fluorine, as a result of continuous application of a transverse field of 3×10^5 V/cm. The source-drain voltage was 0.25 V and the temperature 65 °C. The implant doses are for (B) 5×10^{14} cm^{-2}, (C) 1×10^{15} cm^{-2}, (D) 5×10^{15} cm^{-2}, and (E) 0 cm^{-2}.

TABLE II. ON-current (A) decay due to heat treatment.

	Unimplanted specimen	F-implanted specimen
Before treatment	2.5×10^{-5}	2.3×10^{-5}
After treatment	1.3×10^{-5}	1.8×10^{-5}

IV. DISCUSSION

As can be seen in Fig. 4, the density of gap states N_F decreases due to a low-dose F implantation. However, at a dose above 5×10^{15} cm^{-2}, the defect density in the film does not improve. The presence of an optimum can be ascribed to the competing processes of the reduction of existing defects by the highly electronegative F atoms and the introduction of new void states and point defects created by the bombardment which could not be completely removed by the annealing treatment. Note that the values plotted in Fig. 4 represent an upper limit for the density of states, because the calculation yields an overall value averaged from the Fermi level to the onset of the conduction-band tail which, in addition, includes the interface states. The method is, therefore, relatively unsensitive to the particular position of the intrinsic Fermi level. The above characterization does not preclude that the fluorine is active in passivating interface states rather than bulk states. As both interface and bulk states determine the performance and stability of the device, a distinction has not been made in this study. This is the first time that implantation of monovalent species in plasma-deposited *a*-Si:H is shown to be successful in reducing band-gap defects.

There are two possible origins for the increasing series resistance with increasing F content as observed in Fig. 3. On the one hand, a small fraction of the implanted fluorine atoms could act as interstitial acceptors,[13] thereby compensating the *n*-type doping activity of the phosphorus atoms at the source and drain contacts. On the other hand, the fluorine inclusion could suppress the aluminum diffusion, which should take place during the post-metallization annealing step. This is in agreement with the distinctly smaller diffusion constants for impurities in *a*-Si:F:H as compared to *a*-Si:H.[27] Consequently, a contact barrier with a barrier height dependent on the F concentration persists at the source and drain contacts.

The F-implanted material shows enhanced resistance against every kind of stressing condition. First, the data in Figs. 6 and 7 demonstrate that the Staebler–Wronski effect in the F-implanted material is much smaller than in the unimplanted material. Second, there exists another type of degradation in TFTs due to bias stressing in the dark which causes a slow creation of metastable states near the insulator interface.[28] Even in TFTs with the gate insulator made of amorphous-silicon nitride, this phenomenon can be distinguished from slow charge trapping.[29] The results in Figs. 8 and 9 show that the resistance against field-induced degradation improves with increasing F content. As it is unlikely that F implanted into the active layer influences the kinetics of possible charge trapping in the dielectric, it is justified to conclude that the intrinsic stability of the amorphous silicon has improved. The results then imply that F-implanted *a*-Si:H is less susceptible to field-induced dangling bond generation. This is the first report on the field-induced instability of fluorinated amorphous silicon. Third, the implanted material shows better resistance against heat than the unimplanted material.

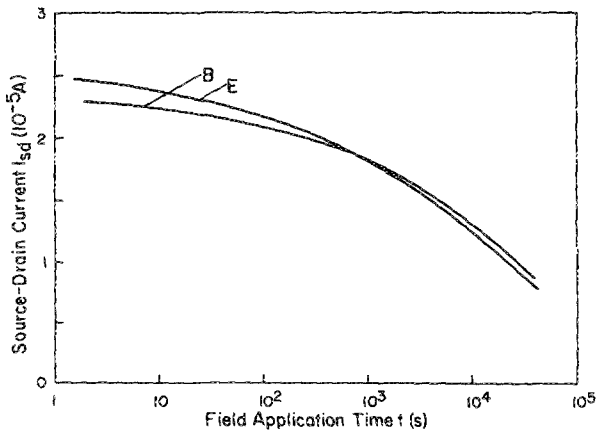


FIG. 9. Decrease in the ON-current of a device implanted with 5×10^{14} cm^{-2} F ions and an unimplanted device.

The results presented in this paper demonstrate that fluorine has a beneficial role in the amorphous network, even if it is implanted in *a*-Si:H deposited from a pure SiH_4 plasma. This suggests that in optimizing amorphous silicon one is not solely dependent on the facilities of changing the deposition process (i.e., the gas-phase precursors). The results represent basic observations. Further studies on the implantation with respect to dose, energy, and substrate temperature during implantation may bring about further optimization.

From our investigations, it is evident that F is effectively built-in in the *a*-Si:H network. The amount of fluorine in our films is at most 1%. This is in agreement with the effectiveness of F at concentrations below 1% in *a*-Si:H:F deposited from SiF_4/H_2 mixtures[12] or in *a*-SiGe:H:F.[11] The stability of the present material is comparable to that of *a*-Si:F:H films deposited from intermediate SiF_2 gas and H_2,[30] which showed a $\sigma_{phB}/\sigma_{phA}$ ratio of 0.5 after a light exposure equal to our exposure in intensity and duration. The heat resistance of the implanted material appears to be intermediate between material deposited from pure SiH_4 and from pure SiF_4.[31]

A possible mechanism for the increased stability could be the blocking of H movements by the presence of F. It has indeed been reported that the diffusivity of impurities is much smaller in *a*-Si:F:H than in conventional *a*-Si:H.[32] This reduced impurity diffusion could also apply to H motion. If we further assume that all metastable phenomena are related to mobile hydrogen, as has been brought forward,[33] the presence of F could block metastable transitions. As observed here, these transitions are then retarded in both directions.

V. CONCLUSION

This work demonstrates that implantation of *a*-Si:H with fluorine can have beneficial effects, thus it provides an

answer to the question of whether the presence of fluorine in the material improves the material quality. Although the initial density of states of the implanted devices is at most a factor of 2 lower than that of the unimplanted devices, the increase in the density of states due to light soaking is considerably less. The implanted material also shows a better resistance against prolonged electric field application and heat exposure.

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