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Optical absorption and photoluminescence of glow-discharge amorphous Si:F films

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Optical absorption and photoluminescence (PL) spectra of fluorinated and hydrogenated glow-discharge amorphous silicon films were measured in the photon-energy range $0.7 \leq h\nu \leq 3.0$ eV. The optical absorption spectra of the fluorinated samples are red shifted by about 0.3 eV, and their band-tail PL peak is red shifted by about 0.4 eV relative to the spectra of hydrogenated samples deposited under similar plasma conditions. Annealing of the *a*-Si:F samples increases their spin density and brings up the PL defect peak at 0.6—0.7 eV, without any significant shift of either the optical-absorption edge or the band-tail PL peak. The similarities and differences in the roles of fluorine and hydrogen in the amorphous silicon matrix are discussed.

I. INTRODUCTION

Optical-absorption and photoluminescence measurements provide detailed information about the electronic structure of amorphous semiconductors. In hydrogenated amorphous silicon (*a*-Si:H) the magnitude of the defect absorption—usually dominant at photon energies below 1.4 eV—correlates with the density of dangling bonds in the film.[1,2] The intrinsic absorption depends on the temperature of measurement and on deposition and annealing conditions which affect the topological disorder of the films.[3] Hence, the sharpening of the optical-absorption tail (the so-called Urbach tail) and the blue shift of the optical-absorption edge of *a*-Si:H with respect to that of evaporated or sputtered amorphous silicon have been attributed to a lower degree of site disorder due to the incorporation of hydrogen in the material.[3,4]

Photoluminescence (PL) is particularly sensitive to defect and tail states in amorphous silicon.[5] In high-quality *a*-Si:H, where the optical-absorption edge is at 1.9 eV, the band-tail PL peak appears at about 1.4 eV. (We shall refer to the optical-absorption edge as the photon energy corresponding to an absorption coefficient of $\alpha = 10^4$ cm^{-1}, measured at room temperature. Unless otherwise specified, the PL-peak position is that measured at about 10 K.) Deposition, annealing, or particle-bombardment conditions which affect the position of the absorption edge have a related effect on the position of the band-tail PL peak.[5] Thus, in chemical-vapor-deposited (CVD) *a*-Si films made at 600 °C, or in hydrogen-evolved *a*-Si:H samples, where the optical-absorption edge was reported to be between 1.70 and 1.65 eV,[6-8] the band-tail PL-peak position was found to be between 1.23 and 1.0 eV.[7,8] PL is also sensitive to the density of defects in the material. Dangling bonds quench the band-tail PL peak[5,9] and, particularly in doped *a*-Si:H, give another characteristic peak, usually at about 0.9 eV.[10,11]

Below we present a comparative study of optical absorption and luminescence of *a*-Si:F and *a*-Si:H. The aim of this research is to investigate the effects of a monovalent species on the electronic structure of *a*-Si, in an attempt to evaluate in detail the role of hydrogen in *a*-Si:H that helps to transform amorphous silicon into a useful electronic material. Fluorine is a natural choice for such a comparative study. It is monovalent and it bonds readily to silicon with the same tetrahedral angle of the Si—Si and Si—H bonds.[12] Furthermore, the Si—F bond length is 1.53 Å, only 0.06 Å more than the Si—H bond length.[12] Even though fluorine is a larger atom than hydrogen, it achieves a comparable bond length to silicon due to its larger bond energy—5.6 eV versus the 3.1 eV of the Si—H bond.[12] Bonded fluorine apparently does not create any extrinsic defects in the *a*-Si matrix, as is evident from the device-quality material which can be obtained from *a*-Si:H:F, which contains 5—10 at. % fluorine.[13] However, in *a*-Si:H:F one cannot distinguish between the specific effects of hydrogen and fluroine on the electronic structure, which is the object of the present work.

II. SAMPLE PREPARATION AND PROPERTIES

The *a*-Si:F samples were prepared at the Technion by plasma glow discharge of a SiF_2+SiF_4 gas mixture at a pressure of 0.2 Torr and flow rate of 3 sccm.[14,15] (sccm denotes standard cubic centimeters per minute.) Phosphorous doping was obtained by direct sublimation.[13] The samples were produced either by rf glow discharge at substrate temperatures of 225 and 250 °C, or by dc glow discharge at 350 °C.[14] The plasma voltage in the dc case was 530 V, the current 1.2 mA, the interelectrode spacing 2 cm, and the electrode area 40 cm^2. The absolute value of rf power coupled into the plasma was not measured, but the plasma luminosity was similar for the rf and dc cases, so the coupled power is estimated to be below 1 W. The deposition time was $2\frac{1}{2}$ h, and samples thickness varied between 0.1 and 0.7 μm.

The *a*-Si:H sample used for the optical-absorption measurements was prepared at a substrate temperature of 250 °C in an identical plasma reactor.[14] For both types of depositions we used the same gas-flow rates and gas pressures, but the power required to sustain the plasma for the *a*-Si:H deposition was twice that of the *a*-Si:F deposition. Despite the similarity of the plasma conditions, owing to differences in the thermodynamic properties of the silicon-fluorine and silicon-hydrogen plasmas, the *a*-Si:F films had deposition rates about 6 times lower than the *a*-Si:H films, and the amount of incorporated fluorine in *a*-Si:F films was somewhat lower than the amount of incorporated hydrogen in *a*-Si:H films prepared under similar plasma powers, gas pressures, gas-flow rates, and substrate temperatures.[14] The *a*-Si:H sample was deposited from undiluted SiH_4 gas and its optical and electrical properties were similar to those usually obtained by rf glow-discharge deposition at a plasma power below 5 W.[1,9]

The *a*-Si:F samples were deposited on fused silica and contained between 7 and 10 at. % fluorine, as determined by electron spectroscopy for chemical analysis (ESCA), calibrated against a nuclear-analysis technique.[16] ir spectra of the films indicated that at least 80% of the fluorine in the films was bonded in monofluoride form.[14,17] No other bonding forms of fluorine could be identified in the as-deposited films by ir spectroscopy. The oxygen content of the films was below 0.1 at. %, which is the detection limit of the Auger measurement used for this analysis. The spin densities of the films were determined by EPR, calibrated against a Varian strong-pitch standard. The lowest spin densities obtained in the *a*-Si:F samples were about 3×10^{17} cm^{-3},[18] which is about 2 orders of magnitude higher than the spin densities obtained in good-quality *a*-Si:H films,[1,2,5,8,9,19] yet it is 2—3 orders of magnitude lower than one obtains in nonhydrogenated evaporated, sputtered, or CVD amorphous silicon films.[7,20] The amorphicity of the samples was verified by Raman spectroscopy, which did not indicate any microcrystalline grains.[14]

Some of the rf glow-discharge *a*-Si:F films deposited at 225 °C were subsequently annealed at higher temperatures. Annealing was done in the deposition reactor with the plasma power turned off, for a total period of 15 min for each annealed sample. Annealing transformed the fluorine from the Si—F bonds into SiF_4 molecules, which remained trapped in the film.[17,21] It also increased the spin density up to about 3×10^{19} cm^{-3} in films annealed at 630 °C. Similar behavior is observed in *a*-Si:H films.[8,19] However, in the *a*-Si:F films the spin density reached values above 1×10^{19} cm^{-3} already at an annealing temperature of 400 °C. In *a*-Si:H films such spin densities are usually not exceeded before the annealing temperature reaches about 550 °C. As discussed elsewhere, this indicates that the initial stages of fluorine evolution in *a*-Si:F are accompanied by a much lower degree of bond reconstruction than hydrogen evolution in *a*-Si:H.[14]

The electronic-transport properties of the *a*-Si:F films are reported elsewhere.[14] Characteristic values of the room-temperature conductivity, the activation energy of the dark conductivity (as measured between 100 and 200 °C), and the photoconductivity of some of the films reported in this work are given in Table I.

The *a*-Si:H reference sample for PL was deposited at the Xerox Palo Alto Research Center.[9]

III. EXPERIMENTAL DETAILS

A. Optical absorption

Sample absorptance below $A = 0.3$ was determined as a function of wavelength by photothermal deflection spectroscopy (PDS).[2] Depending on sample thickness, PDS was effective at photon energies below about 1.8 eV. The samples were held in liquid CCl_4 and were irradiated (pumped) by a monochromatized, chopped Xe-Hg arc lamp. The probe beam was a He-Ne laser focused at grazing angle with a cylindrical lens. Sample absorptance above 0.1 was measured with a Cary-17 double-beam spectrophotometer. Interference fringes were averaged at half-cycle on a logarithmic scale.

B. Photoluminescence

The photoluminescence was excited with an Ar^+ laser at 5145 Å and detected with a cooled Ge detector. Measurements were made of the emission spectrum and intensity at temperatures between 10 and 200 K.

TABLE I. Electronic properties and PL data of some of the samples (see text). T_d denotes deposition temperature, T_a denotes annealing temperature, N_s denotes spin density, σ_{RT} denotes room-temperature conductivity, ΔE_σ denotes conduction activation energy, $\eta\mu\tau=$ (quantum yield)×(mobility)×(photocarrier lifetime) as derived from steady-state photoconductivity measurements (Ref. 14), I_{PL} denotes photoluminescence intensity relative to an *a*-Si:H sample on a ground glass substrate, E_{PL} denotes band-tail luminescence-peak energy, and NM denotes not measured.

Sample	T_d (°C)	T_a (°C)	N_s (cm^{-3})	σ_{RT} (Ω^{-1}cm^{-1})	ΔE_σ (eV)	$\eta\mu\tau$ (cm^2/V)	I_{PL}(rel.)	E_{PL} (eV)
F221	225		1.0×10^{18}	NM	NM	NM	7.5×10^{-3}	0.93
F222	225		5×10^{17}	2×10^{-10}	0.72	7×10^{-11}	9.8×10^{-3}	1.03
F234	250		1.1×10^{18}	NM	NM	NM	1.2×10^{-2}	1.03[a]
F113	350		3×10^{18}	1×10^{-7}	0.59	NM	NM	NM
F236	250		3.7×10^{18}	NM	NM	NM	2.3×10^{-2}	0.98[a]
F175	225	275	1.3×10^{18}	2×10^{-9}	0.70	1×10^{-10}	4.3×10^{-3}	0.96
F187	225	375	4×10^{18}	1×10^{-7}	0.60	5×10^{-11}	1.7×10^{-3}	1.04
F182	225	475	2×10^{19}	7×10^{-7}	0.52	4×10^{-11}	1.0×10^{-2}	0.97

[a] Samples on grounded fused silica (other samples on plain fused silica).

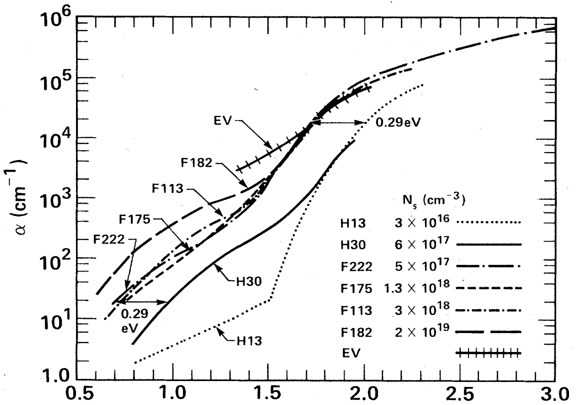

FIG. 1. Optical-absorption coefficient vs photon energy of *a*-Si:H and *a*-Si:F samples of different spin densities. Curve H30 is from Ref. 1. Curve EV gives the absorption coefficient of an ultrahigh-vacuum-evaporated *a*-Si film deposited at an elevated substrate temperature (Ref. 20).

IV. EXPERIMENTAL RESULTS

The optical absorption of some of the as-deposited and annealed *a*-Si:F samples, and of the hydrogenated reference sample, H13, are shown in Fig. 1. The figure also displays PDS data of an *a*-Si:H film deposited at a plasma power of 30 W (curve H30) which had a spin density of 6×10^{17} cm^{-3},[1] and a typical curve of evaporated *a*-Si deposited at 400 °C, which contains 3×10^{19} spins/cm^3 (curve EV).[20]

The dominant feature in Fig. 1 is the almost rigid red shift of the absorption edge of all the *a*-Si:F samples with respect to the hydrogenated samples. Samples F222 and H30, which have about the same spin densities, also have an identical shape of their absorption curves with an almost rigid shift of 0.29 eV with respect to each other over the entire measured spectral range ($0.65\leq h\nu\leq1.9$ eV). The small variation of the absorption-coefficient data of the *a*-Si:F samples above 10^3 cm^{-1} is also remarkable. In fact, all the rf glow-discharge *a*-Si:F films deposited above 200 °C, and all the dc glow-discharge *a*-Si:F films deposited above 275 °C (e.g., all films which contained less than 12 at. % fluorine),[14,21] gave almost identical optical-absorption curves in the absorption region above 10^3 cm^{-1}. These curves all fall between the absorption curves of high-temperature evaporated *a*-Si (Ref. 20) and CVD *a*-Si films which contain less than 1% of either hydrogen or fluorine.[6,22] We should emphasize that sample F182 shown in Fig. 1 contained at most 2 at. % fluorine bonded in the film (the rest was transformed into gaseous SiF_4 molecules by the 475 °C anneal),[14] while sample F113, for example, contained at least 8 at. % fluorine in silicon-monofluoride bonds.[21] This difference is not reflected in the position of the optical-absorption edge and therefore show that, at least at low concentrations, the optical gap is not primarily determined by the fluorine content. This result is somewhat surprising since it was reported that at high concentrations fluorine recedes the valence band of *a*-Si:F with respect to the Fermi energy by about the same amount that hydrogen does, namely 0.22 eV per each 10 at. %.[23] Furthermore, when the fluorine content reaches 66.6 at. % [e.g., $(SiF_2)_n$ is formed], the optical edge is in the uv,[17] so, on the basis of linear extrapolation, one would expect the optical edge of *a*-$Si_{90}F_{10}$ to be blue-shifted by at least 0.2 eV with respect to evaporated *a*-Si. Such a shift is not observed in Fig. 1.

Unlike the behavior of the optical edge, the defect absorption in *a*-Si:F (at $h\nu<1.5$ eV) does vary with the spin density of the samples. However, in the *a*-Si:F films of spin densities $N_s\geq5\times10^{17}$ cm^{-3}, the defect absorption does not seem to scale linearly with N_s, as was observed in *a*-Si:H samples.[1,2] In fact, a lightly annealed film (F175) that had a higher spin density than sample F222 gave a lower defect absorption below $h\nu\sim1.2$ eV, and sample F113, which had an even higher spin density, had lower absorption than sample F222 below $h\nu\sim0.9$ eV. At the point of maximum variation of the absorption data of the undoped films (which is at about 1.0 eV), a total variation of the density of spins by about a factor of 50 produced a total change of the defect absorptance by only about a factor of 4.

In Fig. 2 we show the absorption data of three samples of different phosphorus-doping levels. The defect absorption is seen to increase with doping level, while at the same time the density of neutral dangling bonds decreases, in agreement with what one obtains in *a*-Si:H.[1,2]

Figure 3 shows typical PL spectra of four samples: the *a*-Si:H reference sample (H137), an *a*-Si:F sample deposited at a substrate temperature of 225 °C (F222), an *a*-Si:F sample deposited at 225 °C and annealed at 375 °C (sample F187), and a phosphorus-doped *a*-Si:F sample ($[P]\simeq2\times10^{-1}$ at. %, sample F237). Two peaks are observed with different intensities in the *a*-Si:F samples. The higher-energy peak is near 1.0 eV. Out of ten *a*-Si:F samples deposited or annealed under various conditions which were examined in the present work, this peak was found between 0.93 and 1.04 eV, which is (0.40 ± 0.05) eV lower than the dominant peak position in *a*-Si:H samples (see Table I). The full width at half maximum (FWHM) of

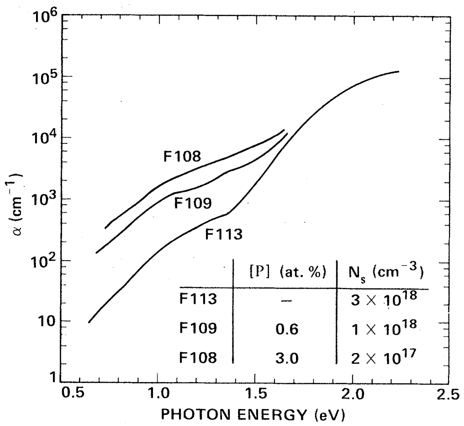

FIG. 2. Optical-absorption coefficient vs photon energy of phosphorus-doped dc glow-discharge *a*-Si:F films deposited at 350 °C. The spin densities are those obtained from the dark ESR signal. The phosphorus content is measured by ESCA.

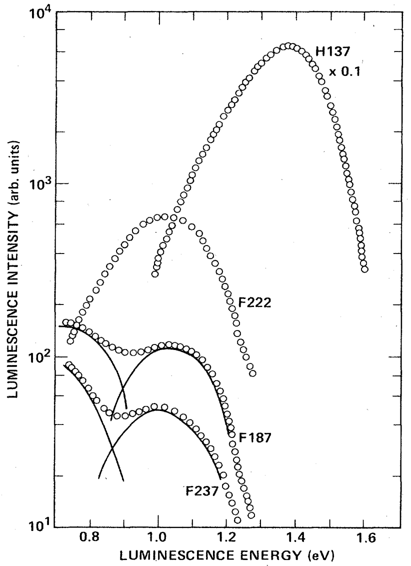

FIG. 3. Photoluminescence spectra of an a-Si:H film (H137), and an as-deposited (F222), 375 °C annealed (F187) and phosphorus-doped (F237) rf glow-discharge a-Si:F films.

this PL band varied between 0.27 and 0.34 eV. No clear correlation was found between the variations of the peak position or PL bandwidth and sample preparation or annealing conditions.

Figure 4 shows the dependence of the position and the magnitude of the 1.0-eV PL peak on the measurement temperature for one of the a-Si:F samples (F236) and the a-Si:H reference sample. In both cases, above 80 K the PL-peak position shifts strongly to lower energies, and the PL signal decays according to an e^{-T/T_0} law.[24,25] The results of Fig. 4, particularly the strong temperature dependence of the peak position,[5] identify the 1.0-eV transition as arising from band-tail states and being, therefore, equivalent to the 1.4-eV peak in a-Si:H. The reduced PL energy is another manifestation of the lower optical gap in a-Si:F.

There are some quantitative differences between the a-Si:F and a-Si:H PL data. In the range 150—200 K, the peak position varies by 2.5×10^{-3} eV/ K for the a-Si:H sample and by 1.8×10^{-3} eV/ K for the a-Si:F sample, and the PL-intensity decay parameter T_0 is 20 and 30 K for the a-Si:H and a-Si:F samples, respectively. The larger value of T_0 has been attributed to a broader distribution of band-tail states, and the associated weaker dependence of the PL-peak position on temperature was explained in terms of an additional temperature-independent band-tail tunneling mechanism which results from the high density of band-tail states.[26] According to this interpretation, the difference in the values of T_0 obtained from Fig. 4 indicates that the width of the a-Si:F band tails is larger than that of the a-Si:H band tails by about 50%. This difference in band-tail width is smaller than what we calculated on the basis of the comparison of the photoinduced absorption and the photoconductivity of a-Si:H and a-Si:F.[27] It is consistent, though, with the difference in the slopes of the absorption-coefficient curves seen in Fig. 1 at $10^3 \leq \alpha \leq 10^4$ cm^{-1} for sample H13 and the a-Si:F samples.

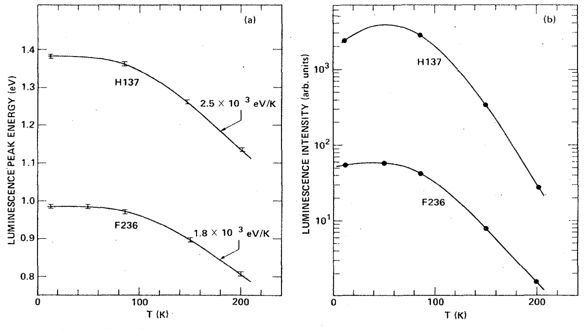

FIG. 4. (a) Photoluminescence-peak position and (b) photoluminescence intensity as a function of temperature for an a-Si:H (H137) and a-Si:F (F236) film.

The band-tail PL intensity in a-Si:F is roughly 100 times weaker than in low-defect-density a-Si:H. An analogy with the hydrogenated material would attribute the quenching to about 10^{18} cm^{-3} dangling-bond defects, and this is indeed approximately the density measured, yet, the PL intensity of the samples was not a simple function of their spin density. In fact, sample F182 (see Table I), which was annealed and had a spin density of 1.8×10^{19} cm^{-3}, had a PL signal similar to that of the low-spin sample, F222. It is possible that structural inhomogeneity and spin clustering in the high-temperature-annealed samples prevents the quenching of the PL band-tail peak.[9]

The lower-energy PL peak in Fig. 3 is just outside the detector energy range, but from the shape of the spectrum it is estimated to be at 0.6—0.7 eV. This peak is observed in doped and annealed samples, which are the same conditions that give defect PL in a-Si:H. Hence we attribute the peak to the defect transition. In fact, Wilson *et al.*[8] reported the defect PL peak at 0.7 eV in a-Si:H samples whose hydrogen content had evolved and which had an optical gap (1.65 eV) and band-tail PL-peak position (1.00 eV) similar to those of our a-Si:F samples. Both data indicate that the defect peak in nonhydrogenated a-Si is shifted approximately the same amount as the gap. Since the defect PL has been associated with a transition from the conduction band, this implies that as the gap decreases by 0.3 eV, the dangling-bond states move toward the conduction band by 0.2—0.3 eV.

V. DISCUSSION

A. Comparison of the properties of fluorine and hydrogen in a-Si

We shall first discuss the similarities and differences between a-Si:F and a-Si:H, and attempt to evaluate the origin of the differences in the position of the optical edge and PL spectra of the two materials.

Optical-absorption-edge shifts in a-Si:H have been attributed either to alloying effects of hydrogen that increase the gap,[8,23,28] or to structural disorder that decreases the gap.[2,4] Defects alone evidently do not shift the gap, since there are many examples in which *a*-Si:H has a defect density of 10^{18} cm^{-3}, but its PL remains at 1.3—1.4 eV. What then, is, the reason for the decreased band gap and the resultant red-shift of the optical edge and PL peak in *a*-Si:F with respect to *a*-Si:H?

We first consider the possibility that only alloying effects control the optical gap. The *a*-Si:F samples contain 7—10 at. % fluorine. Recent work on hydrogen evolution[8] shows that for a variety of *a*-Si:H samples containing initially between 10 and 20 at. % hydrogen, the spin density of all samples reached 5×10^{17} cm^{-3} when their hydrogen content decreased to (7.5 ± 1.5) at. %.[7] At that hydrogen content, the PL-peak position was (1.09 ± 0.02) eV and the optical-absorption edge shifted to (1.65 ± 0.02) eV—similar to the properties of the *a*-Si:F samples reported here. Hence, one possible interpretation of our results is that, in fact, fluorine and hydrogen play identical roles in the *a*-Si matrix, but that a smaller amount of fluorine is incorporated in the *a*-Si:F films than there is hydrogen in *a*-Si:H films, due to differences in the plasma reactions. However, the counterexamples to this model are several reports which indicate that, at hydrogen-concentration levels between 3 and 9 at. %, the optical-absorption edge of *a*-Si:H appears between 1.80 and 1.88 eV,[29] which is well above the optical-absorption edge of *a*-Si:F containing a similar amount of fluorine. As far as we know, the evolved material is the only case in which a substantial hydrogen content results in a low gap.

Cody *et al.*[3] have shown that there is a correlation between the optical gap and the disorder as measured by the slope of the Urbach tail. The *a*-Si:F absorption results, in fact, agree with their data, which is not surprising since they include hydrogen-evolved samples. We therefore propose that the main difference between the two materials is that hydrogen removes strained bonds, reducing the disorder, whereas fluorine does not. To give a plausible argument for this model, we recall the previous observation, namely, that in the low-defect *a*-Si:F films deposited at 200—225 °C, any anneal at a temperature above the deposition temperature was found to increase the spin density of the films sharply. This is different from what one obtains in *a*-Si:H, where a large content of hydrogen may evolve without a significant variation of the spin density.[8,19] The evolution of hydrogen without the creation of dangling bonds is attributed to the considerable reconstruction of Si—Si bonds. This, and other results on the diffusion and evolution of hydrogen in *a*-Si:H, have led to the conclusion that most of the hydrogen in *a*-Si:H is incorporated at positions breaking Si—Si bonds.[30] These bonds reconstruct upon hydrogen evolution. The reduced bond reconstruction upon evolution of fluorine from *a*-Si:F would then suggest that the fluorine atoms are mostly incorporated in isolated Si—F bonds, whose breaking creates nonreconstructed dangling bonds. Hence we suggest that, for a given content of hydrogen and fluorine in an amorphous silicon film, there is a qualitative difference between the type of bonding and the local environment of the fluorine and hydrogen atoms. While hydrogen may break strained Si—Si bonds and form $\equiv$Si—HH—Si$\equiv$pairs,[31] which relaxes the local structure, fluroine seems unable to do so. As a result, the optical gap and PL-peak position of *a*-Si:F are the same as those of *a*-Si which does not contain either F or H.

It seems to us that hydrogen has the unique property to attack and dissolve preferentially strained Si-Si bonds, a characteristic which apparently is not shared by fluorine. For example, studies of deuterated $\mathrm{SiO_2}$ films grown on *c*-Si wafers have shown that a large amount of deuterium (hydrogen) accumulates at the Si-$\mathrm{SiO_2}$ interface and removes gap states from the silicon at the interface region. Secondary-ion-mass—spectroscopy (SIMS) analysis showed that deuterium does not penetrate into the crystalline Si away from the deformed interface region, while in the interface region its density exceeds the density of passivated dangling bonds by a factor of 100.[32] The unique ability of hydrogen to dissolve Si—Si strained bonds may result from the close values of the Si—Si and Si—H bond energies—3.3 and 3.1 eV, respectively.[12] Consequently, hydrogen will attack preferentially strained bonds whose contribution to the free energy of the system is high, yet it would not affect relaxed bonds. Fluorine, on the other hand, has a bond energy of 5.6 eV to silicon.[12] Consequently, fluorine can break any Si-Si bond, and is not selective to strained Si bonds. Thus fluorine gets bonded at random in the *a*-Si matrix. This random bonding is believed to be the reason for the large density of residual strained bonds which cause the red shift in the position of the optical gap of *a*-Si:F.

B. Density-of-states considerations

Figure 5 presents, schematically, the density of states (DOS) of samples H13, H30, F222, and F182 as extracted from Figs. 1 and 3. The general shape of the curves is taken from Ref. 2. The following features can be extracted from the above measurements.

First, as indicated by the red shift of the optical-absorption curves (at $\alpha\geq2\times10^{3}$ cm^{-1}) by about 0.3 eV in *a*-Si:F with respect to *a*-Si:H, the valence band of the *a*-

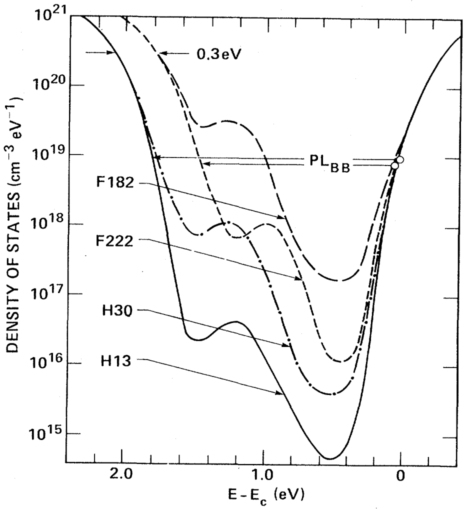

FIG. 5. Schematic diagram of the density of states of *a*-Si:H and *a*-Si:F samples of various densities of dangling bonds.

Si:F samples is closer to the conduction band by about 0.3 eV with respect to the separation of the bands in *a*-Si:H. Comparison of samples F222 and H30 indicates that both the absorption edge and defect absorption have been shifted on the energy scale by the same amount. Assuming that for both *a*-Si:H and *a*-Si:F the defect absorption (in undoped films) is due to transitions from the singly occupied dangling-bond level to the conduction band,[1,33] we find that the dangling bonds shift *rigidly* with the valence-band edge towards the conduction band. The shift of the defect PL of *a*-Si:F with respect to *a*-Si:H by more than 0.2 eV also suggests the same conclusion. Furthermore, in sample F182, where the spin density increased by a factor of 50, the absorption at low energies hardly increased. Possibily the main increase in spin defects occurs at energies further from the conduction band.

The band-tail PL peak of *a*-Si:F was found to be shifted relative to that of *a*-Si:H by about 0.4 eV, which is 0.1 eV more than the decrease of the optical band gap. Assuming similar Stokes shifts for the band-tail PL transitions in both *a*-Si:H and *a*-Si:F, and assuming the PL peaks in both *a*-Si:H and *a*-Si:F correspond to transitions between levels of similar values of the density of states, we may conclude that the larger shift of the PL peak is due to the wider band tailing in *a*-Si:F with respect to that of *a*-Si:H.

V. CONCLUSIONS

We have presented optical-absorption and PL data which shows that, in glow-discharge *a*-Si:F with a spin density of 5×10^{17} cm^{-3} and a fluorine content between 7 and 10 at. %, the optical gap is smaller by about 0.3 eV, and the band-tail PL peak appears 0.4 eV lower than the corresponding values in good-quality *a*-Si:H. In fact, the optical properties are very similar in as-deposited *a*-Si:F, and in *a*-Si deposited at a similar temperature which does not contain either hydrogen or fluorine. The difference between *a*-Si:F films of low spin (as-deposited) and of high spin (fluorine-evolved) showed up mainly in the increase of defect absorption and in the magnitude of the PL defect peak, but not in the position of the optical-absorption edge or the position of the band-tail PL peak. Based on the idea that the variations of the optical gap in *a*-Si are the result of differences in site disorder and the presence of strained bonds, we have suggested that fluorine differs from hydrogen in its inability to relieve the interatomic strain in *a*-Si. We have suggested that hydrogen relieves strained bonds because it is incorporated in locations where it breaks strained (weak) Si—Si bonds. This property may not be shared by fluorine, probably because of the high energy of the Si—F bond, which may cause a random bonding of fluroine in isolated Si—F bonds with no particular selectivity to strained Si—Si bond sites. Finally, we suggest that, in both *a*-Si:F and *a*-Si:H, the singly occupied dangling-bond level seems to peak at the same energy from the valence band.

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