Evidence for Lattice-Mismatch–Induced Defects in Amorphous Semiconductor Heterojunctions

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The size and distribution of built-in electric fields in a-Si:H/a-SiN$_x$:H layered amorphous semiconductor materials have been determined by use of electroabsorption spectroscopy. Strong asymmetries are present between the interfaces, leading to internal fields as large as 4×10^5 V/cm in material with thin (12 Å) layers. These fields are due to an interface charge present when amorphous silicon is deposited onto silicon nitride, which we attribute to strain-relieving defects caused by structural mismatch.

Interfaces between amorphous semiconductor materials are present in a wide variety of electronic devices. However, the structural and electronic properties of these heterojunctions are poorly understood compared to crystalline ones, perhaps because of their greater complexity. Recently, layered amorphous semiconductor structures have been synthesized[1] which exhibit many properties similar to crystalline superlattices,[2] including quantum carrier confinement.[1,3] These materials have conductivity, luminescence, and x-ray scattering properties which indicate that the interfaces are relatively defect-free and smooth on an atomic scale. Because of the large number of interfaces, these structures provide an opportunity to study the interface between two amorphous semiconductors in more detail than was previously possible. In this Letter we report measurements of built-in electric fields in these layered structures obtained from electroabsorption spectroscopy. Large electric fields (up to 4×10^5 V/cm) are present, with the sign of the fields alternating between layers. These fields are caused by electrons, transferred from the nitride to the silicon, which are asymmetrically distributed near the interfaces. The interface charge involved (6×10^{12} cm^{-2}) is similar in magnitude to that observed in silicon nitride films deposited onto crystalline silicon. However, it is greatest when amorphous silicon is deposited onto silicon nitride, and is concentrated within 20 Å of the interface. We attribute this charge to strain-relieving defects induced by lattice mismatch at the interface. In addition, the data show that the band gap changes abruptly at the interface, increasing by more than 0.6 eV in the first 3 Å.

Electroabsorption is the change in optical absorption due to an applied electric field, commonly known in crystals as the Franz-Keldysh effect.[4] Electroabsorption in amorphous semiconductors

has been studied both theoretically[5] and experimentally.[6,7] The effect is a maximum for photon energies near the band gap and decreases sharply at lower energies. In addition to providing spectroscopic information about thin-film materials, electroabsorpton can be used to determine internal electric fields in device configurations. Nonomura, Okamoto, and Hamakawa[8] have measured the built-in potential of n-i-p amorphous silicon solar cells by monitoring the transmission of a film subjected to both a constant and an alternating field. The electroabsorption signal goes to zero when the applied dc field cancels out the internal fields, thereby yielding the built-in potential.

The samples used in this study were made up of alternating layers of amorphous silicon hydride (a-Si:H) and amorphous silicon nitride (a-SiN$_x$:H) deposited by plasma-assisted chemical vapor deposition of silane and silane:ammonia (1:5 by volume) mixtures.[1] The plasma was not interrupted between layers. Silicon layer thicknesses varied between 8 and 1200 Å. Low–contact-potential contacts were used in a sandwich structure so that contact potentials did not distort the applied electric field.

The materials described here have very high ($\sim 10^{12}$ Ω cm) resistivities perpendicular to the layers. This yields a dielectric relaxation time of roughly 1 s, whereas the modulation frequencies used were typically 1 kHz. The depletion width of bulk a-Si:H at this frequency[9] is expected to be several thousand angstroms, which is greater than the thickest silicon layer used. Under these conditions the applied fields are uniform throughout the material. No change in the results was observed if the modulation frequency was varied between 100 Hz and 100 kHz, or if the dc voltage was applied as a pulse of 3 ms duration rather than ~ 3 s. The data presented here were taken at room temperature, although the results were the same at a sample

temperature of 100 K.

If we make use of the boundary condition that the normal component of the applied electric displacement $D = \epsilon E$ is constant, the field within the sample $D(x)$ is the sum of applied and built-in fields:

$$D(x) = D_{dc} + D_{ac}\cos(\omega t) + D_{bi}(x). \quad (1)$$

Here D_{dc} is the dc component and D_{ac} is the ac component of the applied field. $D_{bi}(x)$ is the built-in field, and x is the distance normal to the layers. The local absorption constant changes as the square of the field[4,5]:

$$\alpha(x) = \alpha_0(x)[1 + KD^2(x)], \quad (2)$$

where $\alpha_0(x)$ is the zero-field absorption coefficient and K is an electro-optic material parameter which varies with photon energy. In a transmission experiment the quantity measured is the change in the spatial average of $\alpha(x)$,

$$\langle \alpha - \alpha_0 \rangle = d^{-1}\int \alpha_0(x)KD^2(x)\,dx, \quad (3)$$

where d is the sample thickness. A lock-in detector was used to isolate $\Delta\alpha_\omega$, the portion of (3) which varied at the frequency ω. Because the band gap of a-SiN$_x$:H is ~ 4 eV, we can assume that the silicon nitride layers contribute negligibly over the photon energy range studied (1.2–3.0 eV). If we assume that all silicon sublayers are identical, simple electrostatics gives the change in absorption in terms of the applied voltages V_{ac} and V_{dc}:

$$\Delta\alpha_\omega \sim \alpha_{s0}K_s V_{ac}\left[\phi_s - \frac{V_{dc}}{N}\left(1 + \frac{L_n\epsilon_s}{L_s\epsilon_n}\right)^{-1}\right]. \quad (4)$$

Here α_{s0} and K_s are the absorption and electroabsorption constants of a-Si:H, and N is the number of layer pairs. The sublayer thicknesses are L_s and L_n for the a-Si:H and a-SiN$_x$:H layers, and the dielectric constants[10] are $\epsilon_s = 12\epsilon_0$ and $\epsilon_n = 7.5\epsilon_0$. This equation gives the built-in potential across a single silicon layer, $\phi_s = \int_0^{L_s}(D/\epsilon_s)\,dx$.

Figure 1 shows $\Delta\alpha_\omega$ plotted against V_{dc} for two films with V_{ac} as a parameter. The linearity with respect to V_{dc} and V_{ac} expressed in (4) was obeyed to within experimental error (3%). The $V_{dc} = 36$ V intercept of the lines in Fig. 1 is equal to $\phi_s N (L_s\epsilon_n + L_n\epsilon_s)/L_s\epsilon_n$. This intercept varies from film to film as the thickness and potential change, and was as high as 72 V. This is much too high to be accounted for by a contact effect. Films of the same layer thickness but varying in total sample thickness from 0.2 to 4 μm yielded the same ϕ_s within 20%.
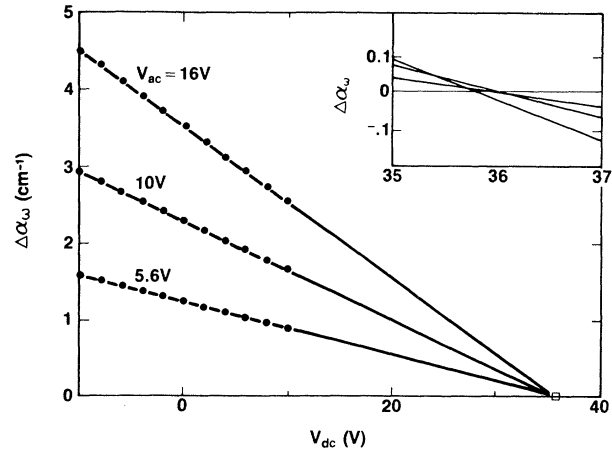

FIG. 1. Electroabsorption signal vs dc voltage for a Si/SiN$_x$ superlattice with layer thicknesses $L_s = 20$ Å for silicon and $L_n = 27$ Å for nitrides; sample thickness, 1.0 μm; photon energy, 1.94 eV. The lines are a least squares fit to the data points. Inset: an expanded version of the x intercept of those lines.

The built-in potentials can only be caused by charges which are asymmetrically placed within the sublayers so that reflection symmetry is absent in the material. Their existence shows that the order of deposition determines the properties of the interfaces. Such a dependence could be caused by ammonia which is outgassing from the walls of the chamber during deposition of the silicon layers. Measurements of the plasma emission spectra during deposition show that the ammonia concentration decreases to less than 1% of its previous level in a monolayer after the gases are changed. In addition, it is not clear how nitrogen contamination could cause charges which would result in built-in fields, since N tends to alloy in a-Si:H rather than dope.[11] An a-Si:H sample prepared here with 5% NH$_3$ in the discharge had a defect concentration of only 3×10^{17} cm^{-3} as measured by sub-band-gap optical absorption. Such a concentration is insufficient to cause the built-in fields observed.

We attribute the field asymmetry to structural defects created during the deposition. Silicon differs greatly from silicon nitride in both crystal structure and lattice constant. This structural mismatch causes strain at the interface which is relieved, as the material grows, through the introduction of defects.

It is known that these materials are proximity doped by electrons transferred from the nitride layers to the silicon layers.[12] Thus we assume that the charges causing the built-in fields are negative in the silicon and positive in the nitride. The signs

of the built-in fields observed here imply that more charge is transferred at the interface where silicon is deposited onto silicon nitride (silicon-on-nitride interface) than at the nitride-on-silicon interface. Because our technique is sensitive only to the difference between the two interfaces, we assume that all charges reside near the silicon-on-nitride interface.

When silicon is deposited onto silicon nitride, any defects are primarily in the silicon because it is easier to introduce defects into the silicon as it is growing than it is to introduce them into the already-grown nitride. If the defects are similar to the dangling-bond defect in bulk a-Si:H, they would be negatively charged in this n-type material. It is reasonable to expect that the defect density would decrease with the distance from the interface. From the change in built-in potential as the sublayer thicknesses are varied, we can roughly determine the actual distribution of charge near the interface.

Assume a density of traps in the silicon layer which decreases exponentially away from the interface according to $n_t = \rho_0 \exp(-x/l)$ for all layer thicknesses. These traps are filled, leaving a positive charge on the nearby interface, as shown in the inset in Fig. 2. This model is compared in Fig. 2 with the results obtained for materials with different silicon layer thicknesses L_s and fixed nitride thickness. Positive ϕ_s designates a field which points away from the substrate. A reasonable qualitative fit is obtained with a defect density of $\rho_0 = 3 \times 10^{19}$ cm^{-3} and exponential width $l = 20$ Å. A decrease in ϕ_s at larger L_s is observed, consistent with the charge-distribution model. However, the built-in potential remains high for low L_s, indicating that the defect distribution is more sharply peaked
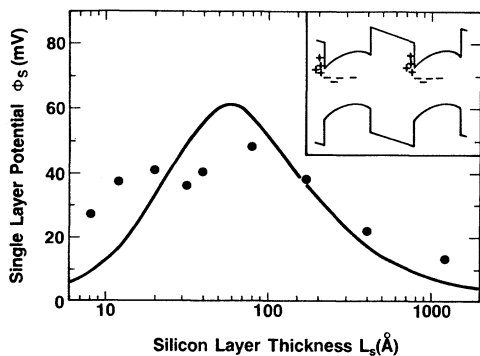
close to the interface than the exponential distribution in the model.

The total interface charge density measured here, $\rho_0 l = 6 \times 10^{12}$ cm^{-2}, can be compared with the surface charge which has been measured when amorphous silicon nitride is deposited onto crystalline silicon. Surface charge densities which have been determined from capacitance-voltage characteristics[13,14] show a charge transfer of the same sign as that observed here, with a density between 1×10^{12} and 6×10^{12} cm^{-2}, depending upon the method of deposition.

Additional information about the interface can be obtained from the spectral dependence of the electroabsorption signal, shown in Fig. 3. The spectrum is similar to that observed from an unlayered a-Si:H sample except for a small band-gap increase due to carrier confinement. The small signal observed at low photon energies ($h\nu < 1.6$ eV) is due to refractive-index changes. The spectral shape observed is the same for all values of V_{dc}. This means that the experimental built-in potential ϕ_s is independent of photon energy, for $h\nu$ as high as $E_g + 0.6$ eV. This verifies that the absorption in the nitride layer is negligible. It also indicates that the band gap changes relatively sharply at the interface between the two layers, for there are no appreciable electric fields in the transition region which would change the electroabsorption signal. In the case of the sample shown in Figs. 1 and 3, the built-in voltage changed with photon energy by less than 10%.
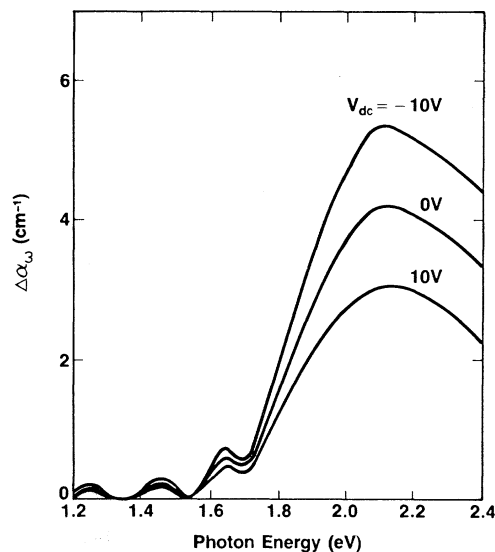
FIG. 2. The variation of the single-layer built-in potential ϕ_s with silicon layer thickness L_s. The nitride layer thickness was $L_n = 35$ Å. Inset: the charge distribution model chosen for the theoretical line drawn.

FIG. 1. Electroabsorption spectrum for sample as in Fig. 1, for three values of V_{dc}. V_{ac} was held constant at 16 V.

With a field of 4×10^5 V/cm at the interface, this indicates that the band-gap shift of 0.6 eV occurs within 3 Å of the interface. This result was observed in all samples studied and is consistent with x-ray scattering results which show essentially atomically abrupt interfaces.[1]

We have determined the built-in electric fields in amorphous semiconductor superlattices using electroabsorption spectroscopy. These fields are surprisingly large in amorphous silicon/(silicon nitride) materials, as large as 4×10^5 V/cm in thin (12 Å) layers. The fields are due to charged structural defects which we attribute to interfacial lattice mismatch. Thus we conclude that the interfaces between lattice-mismatched amorphous materials have interfacial structural defects analogous to misfit dislocations in epitaxial crystalline materials.

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