Charge storage in undoped hydrogenated amorphous silicon by ambient atomic force microscopy

B. Rezek, T. Mates, a) J. Stuchlík, a) J. Kočka, a) and A. Stemmer

Nanotechnology Group, Swiss Federal Institute of Technology, Tannenstrasse 3, 8092 Zürich, Switzerland
(Dated: 3. 6. 2003)

Hydrogenated amorphous silicon (a-Si:H) layers are prepared by plasma-enhanced chemical vapor deposition on metallized glass substrates. Ambient atomic force microscopy (AFM) is employed for both modification and characterization of a-Si:H films. Voltage pulses of up to 35 V are applied as a cantilever scans the amorphous silicon surface in contact mode AFM. Subsequent detection by Kelvin probe microscopy reveals a persistent negative charge stored in a-Si:H layers. The stored charge is always negative independent of voltage polarity and results in upward shift of the Fermi level by as much as 0.1 eV. Only at higher negative voltages (< −15 V) a positively charged oxide layer grows on the surface due to anodic oxidation. A model of the observed phenomena is proposed considering charge transport across a biased contact junction, metastable trapping in bandgap states of a-Si:H as well as influence of silicon oxide.

PACS numbers: 73.61.Cw, 68.37.Ps, 73.50.Gr, 73.40.Cg

Hydrogenated amorphous silicon (a-Si:H) has found wide application in flat panel displays, photovoltaic solar cells, and sensor arrays. These devices benefit from deposition on metallized glass substrates. Ambient atomic force microscopy (AFM) is used for identifying the structure and properties of a-Si:H films as well as for its electronic properties. Specific electronic properties of a-Si:H arise from a lack of long distance order and a large number of coordination defects, which result in a continuous density of electronic states [1].

Various techniques were investigated to find a connection between the microstructure and electronic transport. In contact mode atomic force microscopy (AFM), measurement of surface morphology can be combined with independent, simultaneous detection of local currents by applying a bias voltage to conductive cantilevers [2, 3]. In this manner, transport and structural properties of silicon thin films were directly correlated with very high lateral resolution below 5 nm [4].

Application of a bias voltage in AFM was also found to generate a persistent, spatially localized modification of electronic properties of undoped amorphous and microcrystalline silicon films. In ambient environment, increased sample resistivity was detected and attributed to the formation of a thin oxide layer [5]. In ultrahigh vacuum, decrease in current and contact potential difference was observed and proposed to be connected with metastable charge trapping in defect states in the middle of the energy bandgap [6].

These preliminary studies open new prospects for a-Si:H based devices. Spatially localized charges in silicon thin films could be used to induce self-assembly of particles from colloidal suspensions to the charged patterns, a technology recently developed for fluorocarbon films [7].

In this letter, charge storage in undoped a-Si:H films is systematically studied by ambient AFM as a function of bias voltage magnitude and polarity. Although ultrahigh vacuum allows one to maintain stable and well-defined surface properties, ambient environment is more practical for sample processing and further wet chemical treatment. Modifications of the films are detected by Kelvin force microscopy (KFM) as variations in surface potential. A model for the charge storage mechanism is proposed which considers charge transport across a biased contact junction, metastable trapping in bandgap states of a-Si:H, and the influence of surface oxidation.

Films of 1 μm thick a-Si:H were prepared by radio frequency (13.56 MHz) plasma-enhanced chemical vapor deposition using 8% dilution of silane (SiH4) in hydrogen. A Corning 7059 glass metalized by a nickel–chromium layer was used as a substrate.

Ambient AFM (Multimode Digital Instruments) was employed to probe and modify the a-Si:H films. Highly doped n-type silicon cantilevers (NCH Nanosensors) with a resistivity of 0.010–0.025 Ωcm and a spring constant of 20 – 52 N/m were used. In contact mode AFM, voltage pulses of both positive and negative polarities and varying amplitude (5 – 35 V in 5 V steps) were applied in a 10 × 10 μm square region as a cantilever was scanning the surface. Applied contact forces of ≈ 100 mN ensured good electrical contact [4].

The pulse duration was 10 ms, followed by a 10 ms delay. Taking into account a cantilever scan speed of 0.5 Hz and 256 pixels along a scan line, one pixel is exposed to voltage for 4 ms. The pulse duration is a critical parameter. In undoped a-Si:H the dielectric relaxation time is typically < 1 ms which means that the electric field becomes confined to space charge regions near the tip and bottom contact.

After applying voltage pulses, surface potentials were detected at the same place over a somewhat larger area of 20 × 20 μm using an interleaves technique of KFM [9, 10]. The images of surface potential reflect the contact potential difference (CPD) between the cantilever and

a) Institute of Physics AS CR, Cukrovarnická 10, 162 53 Prague, Czech Republic

Typeset by REVTEX
The CPD is generally determined by surface work functions of the two materials, however, it can be influenced by adsorbate layers formed in a gas ambient.

The work function of cantilevers was calibrated to $4.1 \pm 0.1$ eV on a thermally evaporated gold layer. The surface work function of the latter was obtained from photoemission yield experiments. Adsorbates from ambient may reduce the gold work function by as much as $0.4$ eV [11], thus the value of $4.1$ eV should be considered as merely indicative.

The work function of undoped $a$-Si:H ranges in a closed environment between $4.3$ for fresh and $4.6$ eV for oxidized surfaces, respectively [12]. In ambient humidity (34–37% in our lab) a dipole-oriented water layer can form at the surface and increase the surface work function by approx. $0.4$ eV, as reported for mica substrates [13]. Water molecules are also known to act as electron donors in case of $a$-Si:H [1]. This results in a decrease of the surface work function. Since the excess charge is accommodated in $a$-Si:H gap states the shift of the Fermi level is small, i.e. in the range of $0.1$ eV.

Thus the configuration of tip and sample work functions results in a negative offset of CPD images since in the KFM setup the compensation voltage is applied to the tip. Brighter regions then correspond to smaller CPD which can be attributed to a negative charge in the sample.

Resulting AFM surface morphology and potential images of $a$-Si:H after the series of positive voltage pulses are shown in Fig. 1. In the potential image (Fig. 1b), a region exposed to voltage pulses appears brighter than the untreated areas of the surface. A lateral profile of relative potential differences across this region (Fig. 1c) shows increasing contrast of up to $80$ mV for larger voltages. On the other hand, surface morphology (Fig. 1a) remains unchanged, it is overall populated by small hillocks with average corrugation of $2$ nm (note two trenches due to a scratched underlying electrode). Thus the contrast in surface potential can be attributed only to the accumulation of negative charge in the $a$-Si:H layer. This surprising fact that the sample is negatively charged by positive voltage pulses can be explained as follows.

When the cantilever is in contact with the $a$-Si:H layer a space charge region is formed at their junction. This is illustrated by an energy band diagram in Fig. 2 where work functions of both materials are considered. Evidently, the junction is reverse biased for positive tip voltages. Because each voltage pulse is longer than the dielectric relaxation time, electrons are accumulated in the $a$-Si:H subsurface region and some of them are trapped in deep gap states (dangling bonds) there [14] or they can even generate additional states [15]. In response, the atomic structure re-arranges in the vicinity of the trapped charge due to the flexible amorphous network. Under these conditions, the electron charge persists in the layer because its re-emission probability is very low at room temperature.

Results for a series of negative voltage pulses are shown in Fig. 3. At smaller bias voltages ($> -15$ V) pulsed region is bright in potential (Fig. 3b) and its morphology appears unchanged (Fig. 3a). For larger voltages, a new feature appears: pulsed region darkens in potential and a growth of some layer can be noticed in morphology. Line profiles in Fig. 3c show that the contrast change from small to larger voltages as well as the increase in layer thickness are functions of bias voltage.

For a negatively biased tip the contact junction is forward biased as deduced from the band diagram in Fig.
2. Since the electric field is confined to the contact junction, the injected electrons remain in the subsurface region where they can be trapped metastably, as in the case of positive tip bias. This results in bright CPD contrast. For larger voltages the electron flux induces anodic oxidation of \(a\)-Si:H surface [16, 17], which gives rise to growth of an oxide layer. The oxide layer incorporates a fixed positive charge [18] which results in a dark CPD contrast.

A sequence of CPD images in Fig. 4, which were acquired over a period of 20 min, shows that as a function of time the dark contrast in potential becomes weaker while the bright region increases in intensity. This may be explained by the fact that the electron injection as well as surface oxidation can induce additional defect states near \(a\)-Si:H surface [1, 19]. Without bias voltage, these new states are filled by electrons diffusing into the surface region. Thus negative charge increases there. Note that additional electrons can diffuse into the \(a\)-Si:H film also during subsequent AFM measurements in order to compensate the tip–sample work function difference.

Eventually, the whole modified region becomes bright, only contrast is weaker in the previously dark area. This can be attributed to partial screening of the negative charge in \(a\)-Si:H by positive charge in the oxide layer. The resulting net charge detected by KFM then depends on the density of charges in the oxide and the density of surface states in \(a\)-Si:H.

![AFM surface morphology and potential images](image)

**FIG. 3:** (a) AFM surface morphology and (b) potential images of \(a\)-Si:H after a series of negative voltage pulses (from \(-5\) to \(-35\) V). (c) Corresponding line profiles acquired along the arrows indicated in the images.

After the charge equilibration in the first 20 – 30 min the potential contrast remains stable. The charge patterns were still detected 17 h after preparation.

Study of the influence of humidity on the charge patterns showed that the negative, bright potential contrast is insensitive both to 98% relative humidity and to immersion in deionized water. The positive, dark potential contrast was enhanced after the application of water and then decayed back again.

To conclude, persistent electronic charge patterns were stored in undoped \(a\)-Si:H thin films by means of voltage pulses in contact mode AFM. The stored charge was always negative independent of voltage polarity and resulted in the upward shift of the Fermi level by as much as 0.1 eV. Only at higher negative voltages a positively charged oxide layer grew on the surface due to anodic oxidation and screened partially the \(a\)-Si:H charge. A model of the observed phenomena was proposed where charge transport across a biased contact junction, metastable trapping in bandgap states of \(a\)-Si:H as well as the influence of silicon oxide were considered. The presented results show modification of \(a\)-Si:H electronic properties with high spatial resolution and they can open new prospects for application of \(a\)-Si:H in nanotechnology.
4