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Distribution of hydrogen in low temperature passivated amorphous silicon (a-Si:H) films from neutron reflectivity

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ABSTRACT

Hydrogen plays a critical role in the passivation of dangling bonds in hydrogenated amorphous silicon (a-Si:H) to enable acceptable semiconducting characteristics during operation in devices. Low temperature processing enables fabrication of high performance transistors on flexible substrates such as plastic or stainless steel foils, but also leads to a decrease in the stability of the electronic performance. Generation of defects at the a-Si:H/insulator (hydrogenated silicon nitride, SiN:H) during electrical use due to localized heating will lead to decreased performance unless the dangling bonds are passivated in-situ by residual hydrogen. For this reason, the distribution of hydrogen within a-Si:H may be critical to understanding their aging phenomena. Here the distribution of hydrogen within both a-Si:H and SiN:H layers is probed with sub-nanometer resolution using neutron reflectivity. The hydrogen concentration within the bulk of the a-Si:H (11 ± 2 at.%) and SiN:H (18 ± 3 at.%) agree well with previous reports, but the increased resolution of the neutron measurement is able to identify an approximate three fold increase in the concentration within 2 nm of the semiconductor–insulator interface. This enhanced hydrogen content may act in the short-term as a sink to passivate any dangling bonds formed during operation.

1. Introduction

Hydrogenated amorphous silicon (a-Si:H) is ubiquitous in electronics [1] and is commonly utilized as a semiconductor in display backplanes for consumer flat screen technologies [2,3] and in thin film solar cells [4,5]. The structure and electrical properties of a-Si:H have been examined extensively for more than 40 years [6,7] with the exact properties being strongly dependent upon processing conditions. From a structural perspective, the topological constraints in the amorphous silicon network require incorporation of hydrogen to reduce the density of coordination defects such as dangling bonds [8]. However, the concentration of hydrogen in device quality a-Si:H is 8–10 at.% [9,10], which is significantly larger than that required for passivation of pure amorphous silicon based upon a dangling bond density of approximately 10^{19} cm^{-3} [11]. This excessive hydrogen in a-Si:H leads to local heterogeneities [12] in the hydrogen content within the film and impacts the electronic properties [13] of the material. The nature of the inhomogeneous distribution of hydrogen within a-Si:H has been studied utilizing many different metrologies including proton magnetic resonance [14], small angle neutron scattering [12], small angle X-ray scattering [15], fluctuation electron microscopy [16], and positron spectroscopy [17]. The heterogeneities have been found to be on the order of 125 Å [18] and consist predominately of polyhydride groups that are incorporated around voids in the amorphous silicon network.

Although the distribution of hydrogen within a-Si:H has been determined, these have, in general, focused on relatively thick films on the order of tens to hundreds of microns in thickness. More importantly, the spatial distribution of hydrogen through the thickness of the film cannot be separated from the heterogeneities in the plane of the a-Si:H film. For thin film transistors such as those found in display backplanes, the electric properties of a-Si:H are time dependent due to a positive direction threshold voltage shift, which can lead to fading of pixels in displays over time [8]. The origins of this threshold voltage shift have been attributed to trapping of electronics near the a-Si:H/hydrogenated silicon nitride gate insulator interface [19]. Thus, the morphological structure near this interface is important to understanding the aging characteristics of a-Si:H transistors. This interface is potentially even more important for an emerging application of a-Si:H in flexible electronics. The opportunities afforded for electronics fabricated on flexible, robust substrates such as plastic are in some cases stifled by the limitations imposed by the substrate [20]. One major limitation as related to a-Si:H is the processing temperature afforded by the relatively low thermal stability of most plastics; this has limited the maximum temperature in our previous work utilizing a-Si:H based transistor arrays on plastic substrates for display backplanes to less than 180 °C [20]. However, this decreased

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temperature leads to an increased susceptibility of the a-Si:H to the threshold voltage shift during operation [21,22]. Thus, understanding the nature of the a-Si:H/hydrogenated silicon nitride gate insulator interface may be helpful in providing insight into routes to reduce this undesired effect.

In this work, we seek to examine any spatial heterogeneities through the thickness of a low temperature (180 °C) a-Si:H film. Of particular interest is the structure near the semiconductor–insulator interface due to its role in device operational stability through the threshold voltage shift. Neutron reflectivity (NR) provides a means to non-destructively examine the hydrogen distribution through the film as a result of the large difference in neutron scattering length density between Si and H and the transparency of Si to neutrons. The average concentration of hydrogen through the thickness of a-Si:H and hydrogenated silicon nitride (SiN:H) layers is consistent with previous bulk measurements, but a substantial increase in hydrogen within 2 nm of this interface is found. These results demonstrate that the heterogeneities in the hydrogen content are significantly altered near the buried semiconductor–insulator interface in a-Si:H.

2. Experimental procedure

2.1. Materials and sample preparation

For the NR measurements, thin films of silicon nitride and hydrogenated amorphous silicon were deposited on standard semiconductor grade silicon wafers. The deposition conditions were maintained to be identical to those used for fabrication of thin film transistor backplane arrays on plastic substrates for flexible displays [21]. In this process, the substrate temperature did not exceed 180 °C. Plasma enhanced chemical vapor deposition (PECVD) was used for both the silicon nitride and hydrogenated amorphous silicon. For the sample examined, a nominally 10 nm thick silicon nitride layer was initially deposited on the silicon wafer, followed by deposition of an approximately 50 nm thick hydrogenated amorphous silicon layer in the same vacuum cycle to prevent any oxidation of the nitride layer. The layers were characterized using spectroscopic ellipsometry (J.A. Woollam). The optical properties of both the silicon nitride and a-Si:H layers were identical to those determined for device quality films on plastic substrates used in flexible displays [21]. The mass density of the a-Si:H and silicon nitride was determined gravimetrically using multiple films deposited at the same conditions to be 2.22 ± 0.05 g/cm^3 and 2.17 ± 0.07 g/cm^3, respectively. The uncertainty in these densities was obtained from the standard deviation in the calculated mass density of multiple samples. A convolution of the error in the thickness determined from ellipsometry and mass of the film determined gravimetrically results in orders of magnitude less error than obtained by comparing sample to sample variation.

2.2. Neutron reflectivity

NR measurements using wavelength $(\lambda) = 4.768$ Å and wavelength spread $(\Delta\lambda/\lambda) = 0.025$ were performed at the Center for Neutron Research (NCNR) on the NG-7 horizontal reflectometer at the National Institute of Standards and Technology (Gaithersburg, MD). A schematic of the reflectivity geometry utilized is illustrated in Fig. 1. The neutron beam was reflected from the film/air interface and detected at the specular condition as a function of angle (θ) in absolute reflected intensities (R). Measurements performed as a function of θ, define the scattering wave vector (q) normal to the film, $q = 4\pi\lambda^{-1}\sin\theta$. NR is capable of probing the neutron scattering length density (NSLD) at depths of up to several thousand Å, with an effective depth resolution of several Å. The uncertainty in reflectivity data was calculated from the instrumental resolution. Fits of the reflectivity data are made by a weighted least-squares regression algorithm based upon the Parratt formalism [23] to determine the elastic coherent neutron scattering length density ($Q_c^2 = 16\pi\rho$) profile, where ρ is the scattering length density (SLD). This approach uses successive layers (a box model) of constant Q_c^2 with interfaces smeared by a Gaussian function leading to error function interfacial width profiles [24].

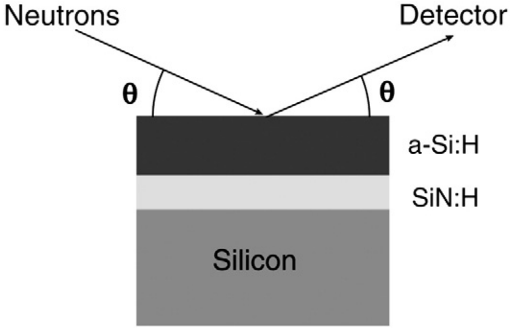

Fig. 1. Schematic of neutron reflectivity geometry and film structure utilized in this study.

3. Results

Fig. 2a shows the reflectivity profiles (symbols) and corresponding fits (lines) for the a-Si:H/SiN:H/Si stack. Two characteristic beating patterns in the Kiessig fringes are evident from the reflectivity data.

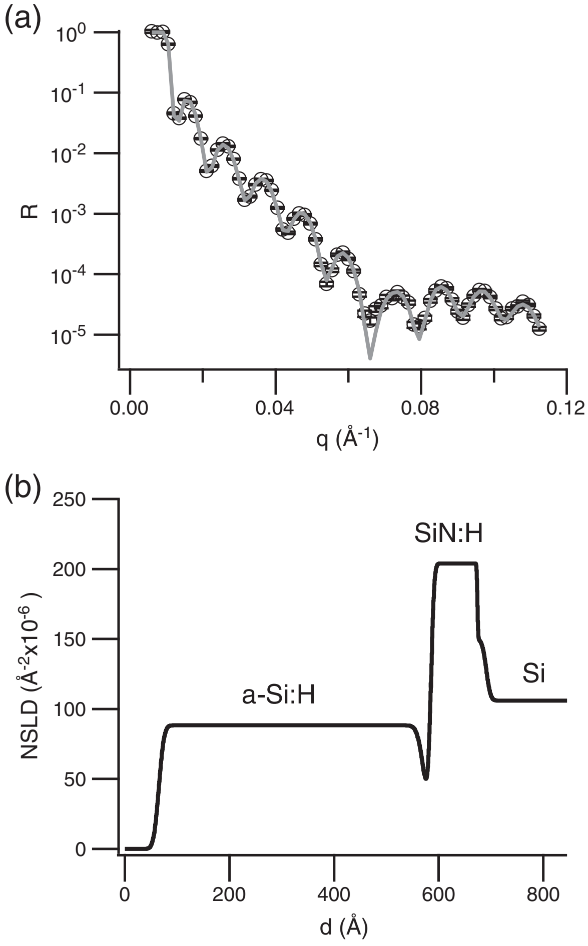

Fig. 2. Neutron reflectivity (a) profile with best fit shown by a solid line and (b) corresponding neutron scattering length density (NSLD) profile corresponding to the best fit. There is a significant decrease in the scattering length density near the a-Si:H/Si_3N_4 interface. The uncertainty in the reflectivity, R, is smaller than the size of the symbol.