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Influence of post-hydrogenation upon electrical, optical and structural properties of hydrogen-less sputter-deposited amorphous silicon

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ABSTRACT

Amorphous silicon (a-Si) is common in the production of technical devices and can be deposited by several techniques. In this study intrinsic and doped, hydrogen-less amorphous silicon films are RF magnetron sputter deposited and post-hydrogenated in a remote hydrogen plasma reactor at a temperature of 370 °C. Secondary ion mass spectrometry of a boron doped (p) a-Si layer shows that the concentration of dopants in the sputtered layer becomes the same as present in the sputter-target. Improved surface passivation of phosphorous doped 5 Ω cm, FZ, (n) c-Si can be achieved by post-hydrogenation yielding a minority carrier lifetime of ~360 μs finding an optimum for ~40 nm thin films, deposited at 325 °C. This relatively low minority carrier lifetime indicates high disorder of the hydrogen-less sputter deposited amorphous network. Post-hydrogenation leads to a decrease of the number of localized states within the band gap. Optical band gaps (Taucs gab as well as E_{04}) can be determined to ~1.88 eV after post-hydrogenation. High resolution transmission electron microscopy and optical Raman investigations show that the sputtered layers are amorphous and stay like this during post-hydrogenation. As a consequence of the missing hydrogen during deposition, sputtered a-Si forms a rough surface compared to CVD a-Si. Atomic force microscopy points out that the roughness decreases by up to 25% during post-hydrogenation. Nuclear resonant reaction analysis permits the investigation of hydrogen depth profiles and allows determining the diffusion coefficients of several post-hydrogenated samples from of a model developed within this work. A dependency of diffusion coefficients on the duration of post-hydrogenation indicates trapping diffusion as the main diffusion mechanism. Additional Fourier transform infrared spectroscopy measurements show that hardly any interstitial hydrogen exists in the post-hydrogenated a-Si layers. The results of this study open the way for further hydrogen diffusion experiments which require an initially unhydrogenated drain layer.

1. Introduction

Amorphous silicon (a-Si) is a common functional material for the production of electronic devices like diodes, thin film transistors (TFTs), liquid-crystal displays (LCDs), optical sensors and solar cells [1–6]. Especially in heterojunction silicon solar cells an intrinsic and hydrogenated a-Si interlayer plays the key role for high efficiencies [6].

A common industrial standard process for deposition of hydrogenated amorphous silicon (a-Si:H) is plasma-enhanced chemical vapor deposition (PECVD). For this kind of process, the flammable and toxic gas silane (SiH_4) is needed.

Silane can be avoided completely by the application of radio frequency magnetron sputter deposition (RFSD). Although it is known since the late 1970s (Refs. [7,8]) that it is also possible to sputter a-Si:H layers, it was only recently published that surface passivation of crystalline silicon (c-Si) substrates by RFS-deposited a-Si:H layers is possible [9–11]. According to these publications the quality of surface passivation of RFS-deposited films was similar to PECV-deposited ones. To achieve surface passivating a-Si:H layers directly during RFSD, Ar has to be mixed with only 2% of hydrogen [11]. More common in the field of RFSD layers for c-Si surface passivation are aluminum oxide (Al_2O_3) (Refs. [12–14]) as well as silicon carbide (SiC_x) (Refs. [15–17]) or silicon nitride (SiN) (Refs. [18,19]).

The usage of the process gas silane in a PECVD reactor allows only deposition of *hydrogenated* a-Si layers. In contrast, RFSD technology

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uses a solid target consisting solely of the material intended to be deposited [3].

Gloger et al. demonstrated that surface passivation of a c-Si wafer by an (i) a-Si:H layer, destroyed by a high temperature treatment, could be recovered by annealing in an atmosphere containing hydrogen radicals [20]. It can therefore be assumed that it is possible to achieve surface passivation by hydrogenating a hydrogen-less a-Si layer in a MIRHP (microwave-induced remote hydrogen plasma) reactor [20]. Analyzing surface passivation of c-Si wafers starting from hydrogen-less a-Si layers allows investigation of hydrogen diffusion within the a-Si layer and the corresponding influence of the amorphous network. An unhydrogenated a-Si layer can also be used as a hydrogen drain layer for investigations like diffusion or effusion analysis of other films or materials, as described e. g. in Refs. [21]and [22]. A thorough knowledge of the characteristics of such a drain layer is of fundamental importance for these investigations.

2. Experimental details

2.1. RF-magnetron sputtering and post-hydrogenation setups

Sputtering of doped (p-type) and intrinsic silicon targets took place in an RF magnetron sputtering system (AJA ATC 2200) at a pressure of 2 mTorr using Ar as process gas. The p-type c-Si target used in this study is doped by boron and shows a resistivity of ~1.6 Ω cm (in-house measured by the 4 Point Probe method [23]). Amorphous silicon films are RFS-deposited on phosphorous doped (n-type, 5 Ω cm, 250 μm, <100> oriented) float-zone (FZ) c-Si wafers with a chemically polished surface. Wafers are dipped in aqueous HF solution prior to RFSD to remove the native silicon oxide. Several samples are deposited varying layer thickness and deposition temperature to investigate the morphology and the influence of the following post-hydrogenation on passivation quality.

Investigations described in Section 3 are based on optimal RFSD conditions with samples prepared at a process temperature of 325 °C and a-Si layer thicknesses of ~40 nm as outlined in Section 3.2.

The post-hydrogenation processes used for the following investigations take place in a MIRHP reactor at a hydrogen pressure of ~1000 mTorr and a temperature of 370 °C [24].

References [24–27] describe the possibility of a post-hydrogenation step of initially hydrogenated (i) a-Si:H by a direct plasma. Tests using a PlasmaLab 100 parallel plate PECVD reactor from Oxford Instruments, applying direct hydrogen plasma, led to a removal of the RFS-deposited a-Si layer within a short time. The chemical stress and the following disorder of Si-Si bonds supported this etching reaction. In case of using the MIRHP reactor, no etching was detected due to the remote plasma operation.

The post-hydrogenation step involves thermal and hydrogen treatment within the period t_t, starting with the ignition of the hydrogen remote plasma and ending with switching off the plasma with immediate unloading of the samples from the MIRHP reactor.

2.2. Passivation quality

Passivation quality and evaluation during post-hydrogenation of RFS-deposited a-Si:H is done by means of effective minority carrier lifetime (τ_{eff}) measurements. These are carried out at room temperature (~25 °C) via microwave detected photo conductance decay measurements (μPCD) using a Semilab WT-2000 with a spatial resolution of 250 μm and bias light of 1 sun. Spatially resolved τ_{eff} data are providing detailed information about the local influence of the post-hydrogenation and the homogeneity of the film. Measurements are cross-checked via τ_{eff} deduction from transient and quasi-steady-state photo conductance decay (WCT 120, Sinton Instruments), also at ~25 °C.

2.3. Microscopic investigation

Microscopic investigations by high resolution transmission electron microscopy (HR-TEM) using a "JEOL JEM-2200FS" yield detailed information about the structure of the sample. Also diffraction patterns are determined by two-dimensional fast Fourier transformation (2D-FFT) for further investigations about the periodicity of the a-Si atoms compared to c-Si [28].

Surface roughness of RFS-deposited (i) and (p) a-Si layers is analyzed by atomic force microscopy (AFM) [29]. AFM analyses are done using an "Asylum Research MFP-3D" in a non-contact mode by scanning a $(1 \times 1)\ \mu m^2$ area with 2^{16} points (256×256).

2.4. Raman investigation

A less extensive examination of a possible crystallization during heat treatment, without the effort of HR-TEM investigations, is Raman spectroscopy [30]. This non-destructive characterization method allows a fast investigation of the Raman-crystallinity. Raman investigations are performed using a "WITec alpha300" with laser wavelength of 488 nm and 100× magnification.

Raman investigation allows determining the presence of amorphous- (a-Si), microcrystalline- (μ-Si), and crystalline silicon (c-Si) on the base of corresponding vibration modes of the Raman shift [3,30]. The uniform bond structure and the limited density of states of c-Si yield a sharp Raman band width of the TO phonon band with a center of 521 cm^{-1}[31]. Losing structural uniformity leads to a TO center shift to lower wavenumbers and a smoothing of the TO peak. μ-Si till example provides a peak center at 510 cm^{-1}[32]. The disordered network of the amorphous structure yields the excitation of other modes. The sharp c-Si TO Raman peak broadens with a center of around 470 cm^{-1}. In addition to this TO phonon band, three more phonon band modes appear:

- 150 cm^{-1} (transverse acoustic, TA),
- 300 cm^{-1} (longitudinal acoustic, LA),
- 380 cm^{-1} (longitudinal optic, LO).

Note that in order to avoid laser induced crystallization during Raman measurements, the laser power has to be below a threshold of 1.5 mW for the sputtered a-Si in comparison to 4 mW of PECVD a-Si [31,33]. The threshold of 1.5 mW is determined by a laser power meter (COHERENT FieldMaster GS) and equates to a power density corresponding to the laser spot size of 0.27 $mW/\mu m^2$.

2.5. Ellipsometry

Determination of the RFS-deposited layer thickness and other optical properties, like absorption coefficient α and determination of the optical band gap E_g takes place using spectral ellipsometry measurements in the wavelengths range from 300–2500 nm (J. A. Woollam V-Vase 2000 ellipsometry unit).

Plotting the absorption coefficient α as a function of photon energy $\hbar\omega$, E_g can be estimated to E_{Tauc} by using Tauc's equation [34–36]. The band gap of amorphous silicon is about 1.8 eV and blurred by defect states without abrupt band edges like c-Si (~1.12 eV) has [37,38]. According to this, a common way estimating the band gap of a-Si is the so-called E_{04} band gap. E_{04} is defined as the energy for which $\alpha = 10^4\ cm^{-1}$[37].

2.6. Hydrogen depth profiling and bonding structures

Nuclear resonant reaction analysis (NRRA) is a powerful, but not a common method, to obtain information about hydrogen distribution with depth in an a-Si layer. Nevertheless, there are some published hydrogen depth profiles of a-Si:H layers measured by NRRA[3,39–41].

NRR-analyses are carried out using a dynamitron tandem accelerator detecting all hydrogen isotopes [42]. Averages of NRRA measured