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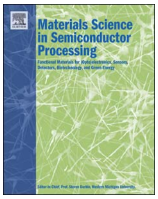

# Lifetime improvement in silicon wafers using weak magnetic fields

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ABSTRACT

We improve the lifetime of *n*-type Czochralski-grown silicon wafers using weak magnetic fields. This processing is found to increase carrier lifetimes by up to a factor of 2, from about 3 μs to 7 μs in our samples. Employing atomic and magnetic force microscopy, surface photovoltage transients, and X-ray photoelectron spectroscopy technique, we show that the effect can be explained by the magnetic field stimulated impurity diffusion from a bulk into the crystal surface, which forms impurity nanoclusters on the surface that can serve as centers of absorption of chemical elements from the environment. This, in turn, increases the oxide film thickness. We furthermore assume that the growth of $SiO_2$ leads to negatively charged oxygen species in the vicinity of the Si/$SiO_2$ interface. The existence of a local electric field generated by the charged areas can thus cause surface gettering by the positively charged metal ions, such as $K^+$, $Na^+$, $Ca^+$, $Al^+$, moved from the wafer bulk. Exposure to weak magnetic fields is therefore assumed to be important for the cost effective overall gettering efficiency during processing of silicon wafers for solar cell production.

## 1. Introduction

Czochralski-grown silicon (Cz-Si) is the mostly important base material for different photovoltaic (PV) and microelectronic technologies [1]. The PV technology has attracted much attention due to clean energy conversion, reliability and infinite abundance of light energy with a comparatively easy installation process [2,3].

The cell efficiency has been gradually improved to a value smaller than ≈25% [4–6], with the theoretical limit of about 29% by solely considering the radiative recombination channel as required by the principle of detailed balance [7]. The conversion efficiency of the Si solar cell can be related to several loss factors such as the ratio of electrons that are not excited to the conduction band per incoming photon, which is often referred to as the optical loss, and that excited to the conduction band but not delivered to outer circuits, which represents the electrical loss [8]. Furthermore, the electrical loss can be further classified into several types, including the loss due to electron-hole recombination as well as scattering of the carriers.

It was long believed that *p*-type Si solar cells were superior to the *n*-type cells [9], have high throughput and can thus dominate the PV industry. Since *p*-type wafers are widely available, their price is cheaper than that of *n*-type wafers. Moreover, the electron mobility in the *p*-type wafers was higher than that in the *n*-type Si. Meanwhile, *p*-type Si has low minority carrier lifetime and light-induced degradation [9], so that high efficiency Si solar cells, such as passivated emitter with rear locally diffused (PERL), heterojunction (HIT) and interdigitated back contact (IBC) solar cells, are made on *n*-type wafers [10]. Of particular importance for demanding structures like IBC solar cells is a documented increase in minority carrier lifetime in *n*-type wafers in comparison with the lifetime observed in *p*-type wafers [11,12]. Further proof of importance in terms of the PV industry is that the *n*-type wafer has higher tolerance to impurities [9].

The minority carrier lifetime is a reliable indicator of the wafer quality. Doping with impurities and high-temperature heat treatments always tend to reduce the minority carrier lifetime. Some types of impurities and defects can be removed from the bulk of a wafer by gettering mechanisms [11], which might improve the lifetime.

The gettering processes redistribute impurities in a specific region of a wafer, e.g. at the surfaces, which can then be either removed by etching, or isolated from the active device regions. In the first case, appropriate techniques are referred to as "extrinsic" gettering. Common examples in Si include metal film deposition, solute diffusion, mechanical or laser damage, ion implantation, polysilicon deposition, corona discharge, Ge-doped Si epitaxy, chlorine or sacrificial oxidation, deposition of $Si_3N_4$ film or porous silicon layer [13]. In contrast, the techniques exploiting internal features such as dislocations, grain boundaries, oxygen precipitates or micro-defects are known as "intrinsic" gettering. This is commonly used in microelectronics and information technology (IT) industry [14–16] where a large portion of the wafer is electronically isolated from the device, a situation that rarely occurs in solar cells.

In the last decade, new approach to controlling electronic processes

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in semiconductors has been proposed based on the application of magnetic fields. Recently, much research has been devoted to magnetic-field assisted change in the electronic properties of silicon wafers and nanostructures [17–22]. Exposure to magnetic fields can be a cost-effective solution for making silicon an ideal solar-grade and electronic-grade material for microelectronic fabrication facilities. Using a pulsed magnetic field was proven significantly affecting the surface relief profile of Si wafers. Thus, the roughness of the wafer surface can increase significantly, from about 1.3–5.8 nm, as reported by Levin et al. [17].

Despite particular achievements in this field very little is known about the nature of the accompanying effects. In particular, the definite experimental evidence for the involvement of trapping and recombination centers is still lacking and some of the results are largely incomplete and controversial.

The aim of this paper is to present a new method for enhancing the lifetime of silicon wafers. We suppose that exposure to magnetic field speeds up the defect reactions in silicon with a subsequent modification of the subsurface structure. The resulting occurrence of electric fields can cause surface gettering by charged ions moved from the wafer bulk.

## 2. Experimental

The experiments were performed using both an electronic grade silicon, which was used to fabricate semiconductor chips, and a solar grade low-quality monocrystalline silicon, originating from impure Czochralski ingots. The wafers obtained with standard Cz technique had double-side-polished surfaces. The Si(111) wafers were phosphorus doped to the resistivity of 4.5 Ω cm, having the thickness of ≈500 µm and 1–3 nm thick native oxide on their surface. The concentration of transition metals, such as Cu, Fe, Au, in the wafers approached $10^{16}$ $cm^{-3}$, as determined by secondary ion mass spectroscopy (SIMS) from the depth of a few microns inside the wafer.

Magnetic treatments (MT) of Si wafers were performed by placing the samples in a static magnetic field $B_0$ oriented along the normal to the wafer surface and produced by ferromagnetic plates. The strength $B_0$ was varied from 0.1 to 0.35 T by changing the distance between the poles. The wafers were kept in the measured cell at ambient conditions for more or less prolonged times. For each set of MT conditions, three to five pairs of sister wafers were used. The data from the treated samples and from the control samples were each averaged to produce two data points, one for MT and one for the reference. It was previously reported that, varying both the strength of magnetic fields and the length of time when the field was applied, the field-induced changes in various silicon parameters saturate at $B_0 \approx 0.2$ T and the magnetic treatment time $t_{MT}$ ranging from 7 to 10 days [23,24]. Keeping all of these considerations in mind, here we restruct our consideration to the lifetime effects observed at $B_0 = 0.17$ T and $t_{MT} = 7$ days.

Atomic force microscopy (AFM) and magnetic force microscopy (MFM) measurements were performed under ambient conditions using a commercial instrument (NT-MDT NTEGRA Prima Scanning Probe Microscope). The topographic and magnetic images were obtained using the two-pass (tapping/lifts mode) technique [25]. In the first pass, the surface profile was imaged in the tapping (intermittent contact) mode [26]. The magnetic structure of the sample surface was mapped in the second pass, when the magnetic sensor tip scanned the previously measured topographic profile at an adjusted distance (lift-height) in the range from 10 to 100 nm above the wafer surface. The magnetic image was obtained by measuring the phase shift of vibrating cantilever at its first flexural resonance, which varied with changing the magnetic tip–sample interaction forces. The tip-sample magnetic interactions were therefore used to reconstruct the magnetic structure of the sample surface.

Surface photovoltage (SPV) transients were measured in the capacitor arrangement using a red light-emitting diode as an excitation source. Details of our setup are given elsewhere [27]. A parallel plate capacitance was formed between a metal grid electrode and the wafer, separated by a mica insulating foil with a thickness of about 20 µm. A 1 GΩ load resistor, a high-impedance buffer cascade based on a field-effect transistor and a sampling digital oscilloscope were used in the measurements. The scanning SPV setup, which provides wafer maps of both the SPV magnitude and decay time with a 100 µm spatial resolution, was discussed by Nadtochiy et al. [28]. A sequence of SPV transients was averaged up to $10^4$ times.

X-ray photoelectron spectra (XPS, EC-2402 spectrometer) were recorded using a monochromatic Mg Kα radiation (energy 1253.6 eV, X-ray source power 200 W), an energy analyzer PHOIBOS-100-SPECS, an ion source IQE 11/35 and a Flood Gun FG 15/40 for compensating the surface charge. The energy resolution of the analyzer was set to 0.1 eV. The X-ray penetration depth was $\approx 10^5$ нм at a photon energy ranging from 1.2 to 1.5 keV. The data were acquired with photoelectron escape depths ranging from 2 to 5 nm at the kinetic energy varying from 1 to 2 keV. Individual Si 2*p* peak components with the full width at half maximum (FWHM) of 1.2 eV in Si and 1.5 eV in $SiO_2$were decomposed using a Gauss-Newton method. The background was subtracted from the raw XPS signal using the method described by Shirley [29].

## 3. Experimental results and discussion

In our experiments, a weak external dc magnetic field with $B = 0.17$ T was applied to Si crystals during $t_{MT} = 7$ days, and the

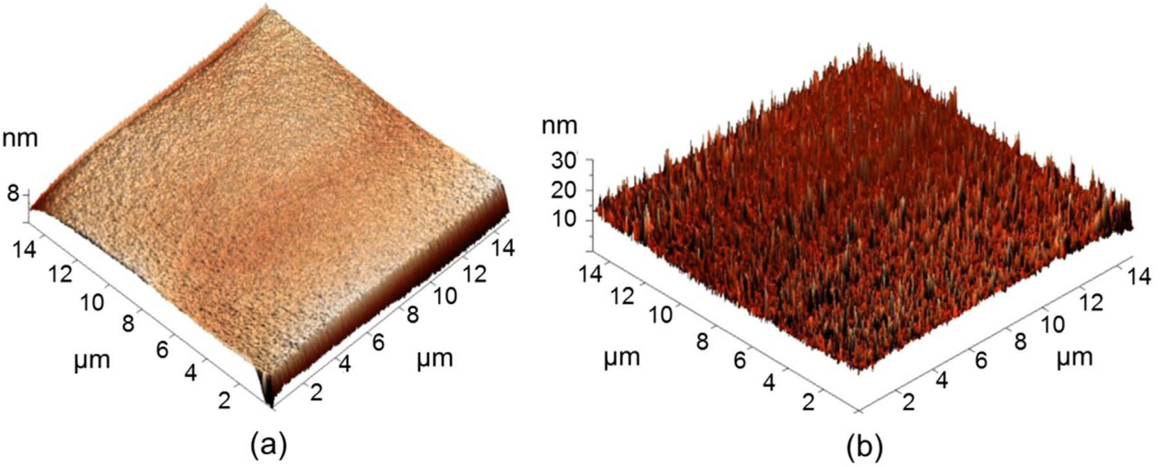

**Fig. 1.** AFM images of the same *n*-Si surface taken before (*a*) and just after (*b*) MT with $B_0 = 0.17$ T during $t_{MT} = 7$ days.