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# Effects of Ultrasonic Cleaning on Carrier Lifetimes and Photovoltage in Monocrystalline Silicon

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**Abstract.** Effects of a kHz-frequency ultrasonic cleaning of silicon wafers on free carrier lifetimes and the photovoltage magnitude are addressed. It is found that the initial photovoltage decay, taken before ultrasonic treatments, can be fitted to a double-exponent form, exhibiting the involvement of shorter- and longer time recombination and trapping centers. The decay speeds up remarkably due to the treatment, and the rapid component of the decay grows at the expense of the slow component. It is also found that, before the treatment, the decay time is markedly non-uniform over the wafer surface, implying the existence of distributed sites affecting carrier lifetimes. The cleaning causes an overall smoothening of the lifetime distribution, which is accompanied by the above shortening. A likely explanation of the effects is based on two facts: (i) the cavitating bubbles are capable of locally removing the surface oxide layer affecting the dangling bonds on the bare Si surface, and (ii) the oxygen and hydrogen, decomposed in water at elevated pressures and temperatures occurring inside a cavitating bubble, can micro-precipitate the Si wafer thus affecting the recombination rate.

## Introduction

It is well known that employing non-renewable fossil fuels contributes to the air pollution and huge climate alterations due to the global heating effect. Based on this fact, using clean energy supplies for heating and generation of electrical power gradually becomes more and more common. Utilizing environmentally friendly natural resources for creating power, and turning to the replenishable and clean electrical power resources may be of a tremendous importance for fighting against global warming thus preventing an androgen climate change.

With regards to clean electrical power sources, wind power is probably most directly suitable for generating electricity, and this is done by tapping the kinetic energy of the wind. Meanwhile, wind power itself is mainly caused by unequal heating of the earth with the sunrays. Moreover, solar power is hitherto one of the most promising renewable energy sources in the world. Because just a tiny fraction of the energy of the sun that hits the earth (hundredth of a millionth of a percent) is enough to meet all our power demands, it is of a rapidly growing demand to get a cheap, efficient and clean converter from light directly to electricity. Therefore, utilizing free energy from the sun, solar cells are now considered to be the best alternative source of electricity.

Currently, industrial production of solar cells is mainly based on doped crystalline silicon (*c*-Si). Both monocrystalline and multicrystalline Si are in use, however, solar cell elements utilizing a single-crystal Si substrate generally have higher conversion efficiencies. Bulk carrier lifetime and surface recombination are very important for the performance of solar cell devices. These parameters are strongly coupled to defects in the crystal which directly affect the performance of any device, e.g. solar cells [1–4]. Recently, research activities in the field of Si photovoltaics exhibit a renewed interest in studying defect reactions with different impurities incorporated into monocrystalline silicon [5]. Among a variety of characterization techniques, the measurement of the spatially resolved carrier lifetime has emerged very recently as a valuable tool for the characterization of silicon wafers and solar cells [6, 7].

One of the most critical operations in processing of Si solar cells is the cleaning of the surfaces of silicon wafers. The complete removal of contaminations and the passivation of rechargeable states on the surfaces are very important issues for improving the energy conversion efficiency of Si cells. Modern wafer manufacturing facilities use various methods of cleaning wafers, which involve pressurized water jet scrubs, rotating wafer scrubbers, wet chemical baths and rinses, etc. Among these methods, ultrasonic treatment is a promising tool to clean Si wafers with the benefit to reduce the application of hazardous chemicals thus preventing dangerous waste [8, 9]. Ultrasonic excitation involves a variety of complex mechanisms, including mechanical vibration and appropriate pressure gradients [10], microcavitation bubbles that oscillate and dance around due to Bjerknes force [11], acoustic streaming flows [12], etc., depending whether liquids are used in the cleaning process or not. In a liquid-filled ultrasonic bath, a typical ultrasonic source is a plane surface attached to the bath flask that oscillates at a single frequency $f$ and produces a longitudinal wave. Acoustic energy is then transmitted to the wafer by the wave which propagates through the fluid.

Wave-induced streaming flows in the cleaning solution, acoustic cavitation, the level of dissolved gases and oscillatory effects are thought to contribute not only to removing particles and complex organic materials from the wafer surface but also modify charged states on the surfaces thus affecting the surface carrier lifetime [13].

In this work, we report the effect of surface cleaning of monocrystalline Si wafers in ultrasonically stimulated distilled water on the spatially resolved carrier lifetime and photovoltage magnitude.

**Experimental**

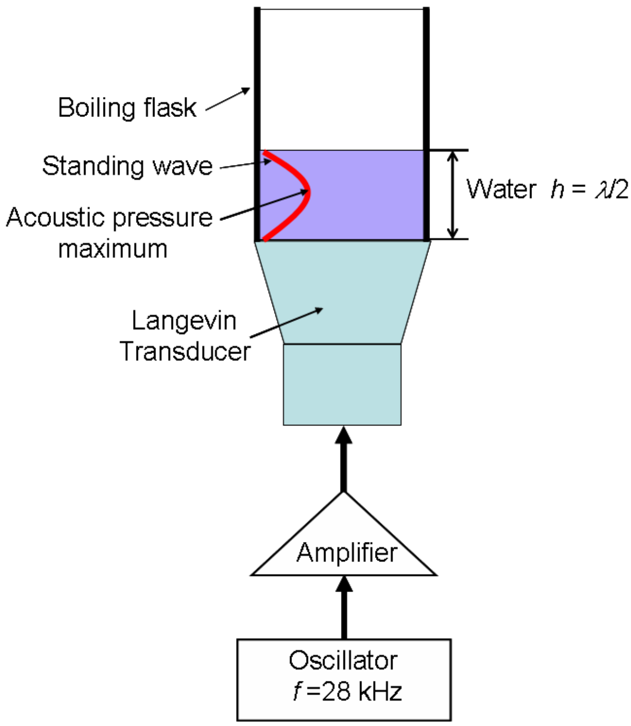


Fig. 1. Schematic of the ultrasonic-based wafer cleaning.

Solar-grade (111)Si:P monocrystalline wafers with a conductivity of 0.5 Ohm·cm and a thickness of 400 μm are sonicated in the distilled water cleaning bath shown in Fig. 1. The main part of the apparatus is a Langevin transducer. When fed with an rf power, it delivers an acoustic power into the water-filled flask with the Si wafer producing a cavitation at sufficiently great driving amplitudes $U_0$. In our measurements, the transducer-water resonance frequency, defined by the water height $h$, is 28 kHz. The temperature of the bulk water was kept between 70 and 80°C during the entire treatment.

Surface photovoltage (SPV) transients are measured in the capacitor arrangement [14], and details of our setup are given elsewhere [15]. A red light-emitting diode is used as an excitation source. The scanning SPV apparatus based on the AC-SPV technique [16] and utilizing a “flying spot” arrangement [17] is used for obtaining spatially-resolved SPV decays. This technique is capable of providing wafer maps of both the photovoltage magnitude and decay transients with a 100 μm spatial resolution.

## Results and discussion

Typical SPV decays taken before and after the cleaning procedure are displayed in Fig. 2 by curves 1 and 2, respectively. It is seen that the initial decay can be fitted to a double-exponent form (dashed line in curve 1)

$$V = V_1 \exp\left(-t/\tau_1\right) + V_2 \exp\left(-t/\tau_2\right), \tag{1}$$

indicating the involvement of several mechanism of recombination and trapping centers resulting in effective lifetimes given by $\tau_1$ and $\tau_2$.

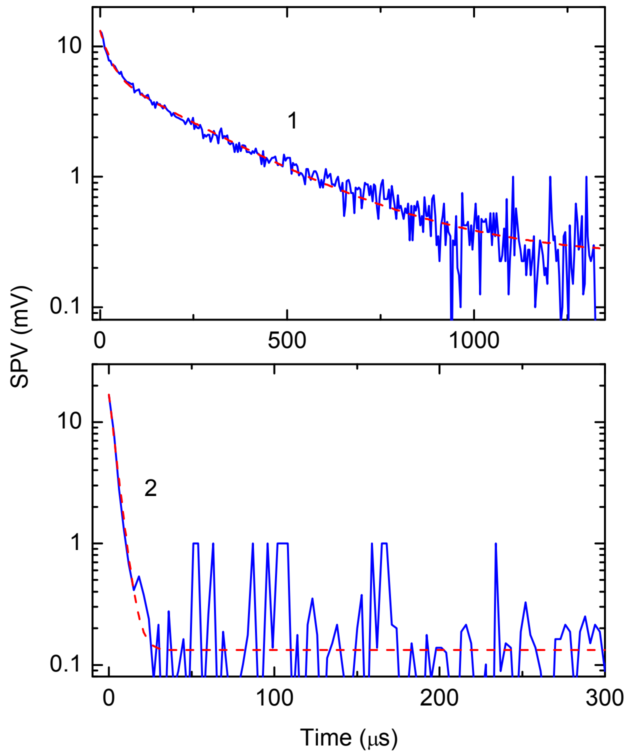


Fig. 2. Semi-log plots of the SPV decays taken in a single point on the surface of the Si wafer before (curve 1) and after (curve 2) ultrasonic cleaning during 30 min. Dashed lines are double-exponent fitting of the decay shapes to Eq. 1.

Ultrasonic cleaning affects the SPV signal rather remarkably, as seen by comparing curves 2 and 1 in Fig. 2. Obviously, the decay speeds up considerably in curve 2, and the rapid component of the decay described by $\tau_1$ grows at the expense of the slow component given by $\tau_2$. This behaviour can be attributed to activation of the air/oxide and oxide/wafer interface dangling bonds, as pointed out previously [13].

More detailed information can be derived by analyzing the spatially distributed SPV signal, which is shown in Fig. 3. The mapped value of $\tau$ is given by $1/\tau = 1/\tau_1 + 1/\tau_2$. It is seen that, initially, the value of $\tau$ is markedly non-uniform [random distribution in the left-hand image of Fig. 3(*a*)], implying the existence of distributed sites affecting carrier lifetimes. The cleaning causes an overall smoothening of the lifetime distribution together with its obvious shortening over the wafer surface [right-hand image in (*a*)]. There also appears a ring structure in the lower part of the right-hand image. This area of the surface is also interesting because it exhibits an enhanced SPV magnitude, which is accompanied by a smoothening of its distribution, as can be seen in Fig. 3(*b*).

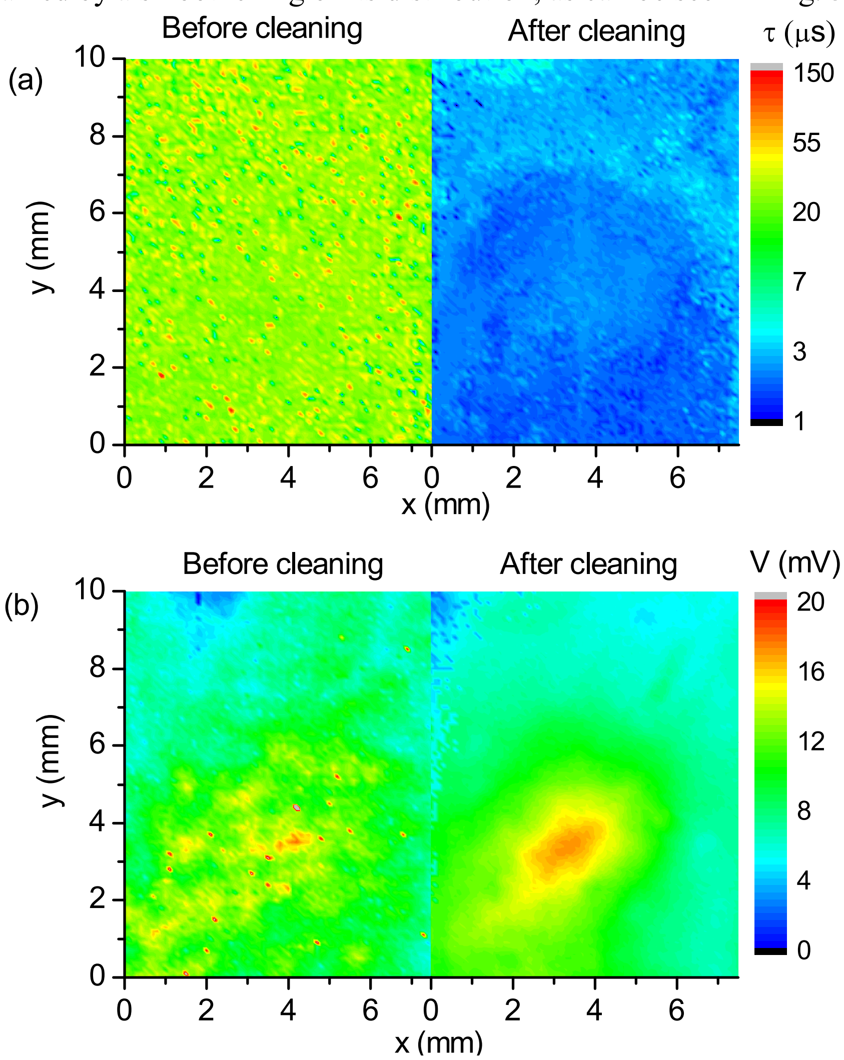


Fig. 3. Spatially resolved SPV decay time $\tau$ given by $1/\tau = 1/\tau_1 + 1/\tau_2$ (*a*) and SPV magnitude given by $V = V_1 + V_2$ (*b*) (see Eq. 1), which are taken over the surface of the Si wafer before (left-hand images) and after (right-hand images) ultrasonic cleaning during 30 min.

The average recombination time $\tau$ can basically be defined as $\tau = \Delta n / R$, where $\Delta n$ is the excess carrier density and $R$ is the recombination rate, and the SPV signal magnitude is $V = (e\Delta n / \varepsilon\varepsilon_0)L$, where $e$ is the elementary charge, $\varepsilon_0$ is the permittivity of free space, $\varepsilon$ is the dielectric constant of Si, and $L$ is the charge separation length. Then one obtains.

$$V = \frac{e\tau R}{\varepsilon\varepsilon_0} L, \tag{2}$$

expressing that decreasing $\tau$ would decrease $V$, if other quantities remain unchanged. It is seen in Fig. 3(*b*) that, although there exists areas in the upper part of the right-hand image which exhibit a decreased $V$, the SPV magnitude increases remarkably within the ring structure. It may therefore be concluded that the cleaning is capable of increasing the recombination rate $R$ in these surface areas.

A likely explanation of the observed changes in the carrier lifetimes and photovoltage can be based on two facts: (i) the cavitating bubbles are capable of locally removing the surface oxide layer developing the dangling bonds on the bare Si surface, and (ii) the oxygen and hydrogen, decomposed in water by the presence of local strain fields and elevated temperatures inside a cavitating bubble, can be trapped at the silicon surface and thus micro-precipitate the Si wafer, which affect the recombination rate. This may be in part due to hydrogen molecules decomposed in water which are mobile in silicon. Since both effects are extremely sensitive to the wafer subsurface morphology, they are non-uniformly distributed across the wafer surface, as observed experimentally and shown in Fig. 3.

## Summary

The ultrasonic cleaning of silicon wafers being an important step in manufacturing solar cells can affect the wafer surface with respect to carrier lifetimes and the photovoltage magnitude. The surface-distributed activation of dangling bonds and surface micro-precipitation are thought to be taken into account in promoting environmentally friendly and non-toxic cleaning steps exploiting cavitation in water solutions.

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