

DEPASSIVATION OF Si-SiO₂ INTERFACE FOLLOWING RAPID THERMAL ANNEALING

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ABSTRACT

The thermal stability of the Si-SiO₂ interface of thermally oxidised silicon wafers is investigated using the Quasi-steady state photoconductivity decay (QSS-PCD) method. Planar silicon (100) and (111), as well as textured (100) wafers with various surface orientations were subjected to Rapid Thermal Annealing. Wafers textured with inverted pyramids displayed the most rapid depassivation rate, while (100) planar wafers showed the slowest depassivation rate. The depassivation rate of wafers which had been textured with inverted pyramids and subsequently rounded by acid etching was between that of (100) planar and wafers textured with inverted pyramids. The results suggest that the Si-SiO₂ interface on planar (100) surfaces is particularly thermally stable, and that the stability gradually decreases as one moves from from a (100) to a (111) surface orientation. The results also suggest that textured surfaces have a lower thermal stability, and a higher recombination rate, that planar surfaces of the same area and surface orientation.

INTRODUCTION

Thermally grown oxide layers are commonly used to reduce the silicon interface state density for passivation of the surfaces of solar cells due to the low achievable interface state densities and low recombination velocities of the Si-SiO₂ interface. If an

antireflection coating is applied on top of a thin layer of SiO₂, such as a layer of silicon nitride deposited by low pressure chemical vapor deposition, then the Si-SiO₂ interface is exposed to high temperatures during the deposition process which can result in depassivation of the interface.

It is known that the interface properties depend, among other factors, on the crystal orientation. In general, (111) oriented surfaces are more difficult to passivate than (100) surfaces. (111) surfaces always display a larger value for the interface trap density D_{it} than (100) surfaces [1,2]. Texturing provides good optical properties for solar cells but may decrease the achievable degree of surface passivation by increasing the surface area and by exposing crystal planes that are inherently more difficult to passivate.

We investigated the thermal stability of the Si-SiO₂ interface for different surface orientations. In order to investigate a range of surface orientations, some (100) wafers were textured using an alkali solution to form inverted pyramids. Some of the textured wafers were then etched in acid solution for 3 or 9 minutes to form surface orientations between (111) and (100).

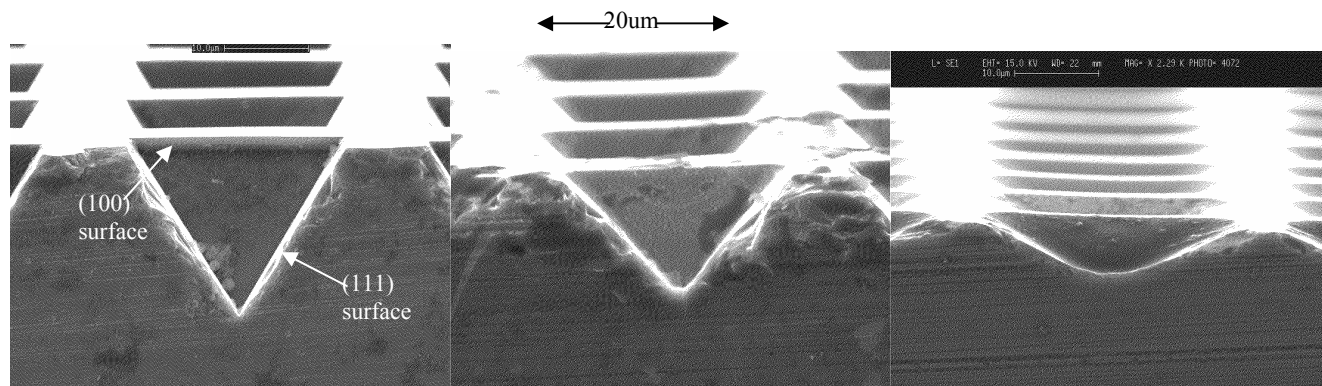


Fig 1. SEM picture of cross section of the etched dot structure

EXPERIMENTAL DETAILS

Float Zoned (FZ), (100) oriented, p-type, 100 Ω -cm, 500 μ m thick wafers and (111) oriented, n-type, 100 Ω -cm, 500 μ m thick wafers were taken as the starting materials. They were initially etched in 10:1 HNO₃: HF solution until shiny. Some (100) wafers were textured to form inverted pyramids. Some of these wafers were subsequently etched in HF:HNO₃ solution for 3 or 9 minutes. SEM pictures of the cross section for these structures are shown in fig 1. Etching reduces the inverted pyramid depth and results in a much shallower texture, with crystal planes between (111) and (100).

After a standard RCA cleaning, selected wafers were passivated with a light phosphorous diffusion (R_s ~ 360 ohm/square after thermal drive in), a thermally grown oxide (~50nm) at 1000°C in dry oxygen with an in-situ N₂ anneal and a 30 minute anneal at 400°C in forming gas (5% H₂ in argon). Isothermal and isochronal annealing was performed in high flow dry nitrogen by Rapid Thermal Annealing (RTA) to test the thermal stability of these structures.

Minority carrier lifetime measurements were made using the quasi-steady state photoconductivity decay (QSS-PCD) technique. For diffused samples, values for the emitter saturation current density J_{oe} were measured at an injection level of 5 \times 10¹⁵/cm². On undiffused samples, the effective surface recombination velocity S_{eff} was estimated from the effective lifetime using PC-1D modeling, assuming a very high bulk lifetime (30ms). This allowed derivation of an empirical equation relating the measured minority carrier lifetime at a particular injection level to the effective surface recombination velocity, S_{eff}, valid for S_{eff} values of no more than ~7000cm/s. The S_{eff} was estimated for the highest measured effective lifetime at in the injection range of 1 \times 10¹⁴/cm² to 2 \times 10¹⁴/cm². This estimation can be applied to our samples if the effective lifetime is greater than 10 μ s.

RESULTS AND DISCUSSION

Fig 2 and Fig 3 show the surface depassivation process of both undiffused and phosphorus diffused samples. Isothermal anneals were done at 550°C from 30 seconds to 360 seconds in nitrogen. On all samples, the rate of increase of S_{eff} or J_{oe} decreases with increasing anneal time. The (100) surface shows the lowest surface recombination velocity and depassivation rate, while textured wafers display the most rapid depassivation. The depassivation rates of the etched samples are between those of the textured samples and the (100) samples. The (111) surface has a depassivation rate similar to that of the sample that was etched for 3 minutes following texturing.

Figures 4 and 5 show the isochronal RTA results. All samples were annealed for 3 minutes in nitrogen. For all the samples, the depassivation rate increases with annealing temperature. Similar to Fig 3 and Fig 4, (100) samples display the slowest isochronal depassivation rate while textured wafers display most rapid depassivation. (111) samples perform similar to the 3 min etched samples.

It is clear that surface orientation plays an important role in determining the surface recombination properties, with (111) surfaces being much more difficult to passivate than (100) surfaces. This may be partly due to a higher defect density at oxidised (111) surfaces, but it appears to be, at least in part, also the result of increased recombination activity of defects at (111)

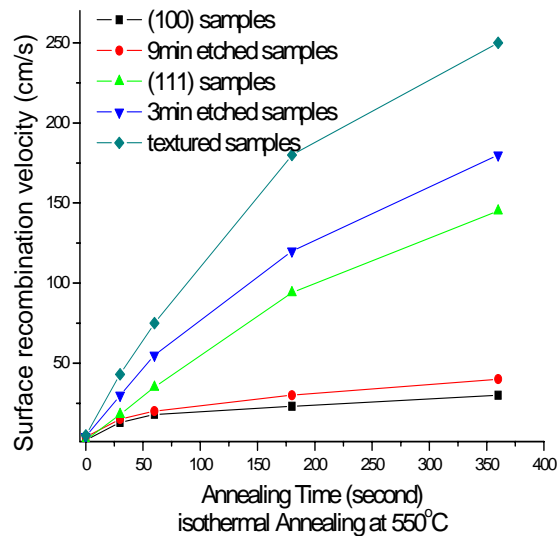


Fig 2: Effective surface recombination velocity S_{eff} vs isothermal annealing time for RTAs

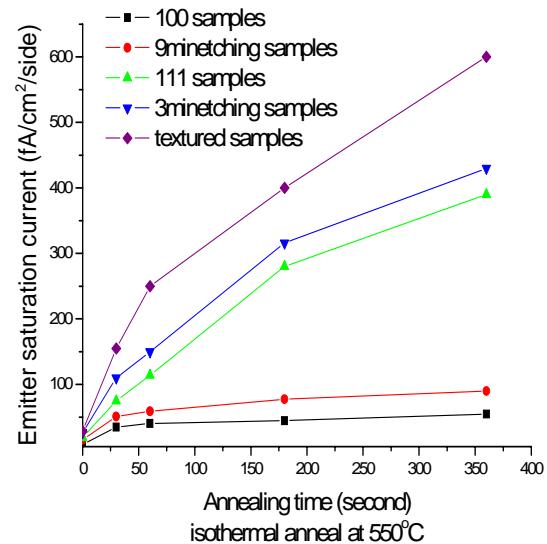


Fig 3: Emitter saturation current (J_{oe}) vs isothermal annealing time for RTAs

surfaces. As another example, in a separate experiment diffused, oxidised (100) and (111) wafers were vacuum annealed at 800°C for 2 hrs to remove all hydrogen from the interface. After this treatment, the J_{oe} of the (111) wafers was an order of magnitude larger than that of the (100) samples while the

difference in defect densities between (111) and (100) surfaces is typically 'only' about a factor of 3.

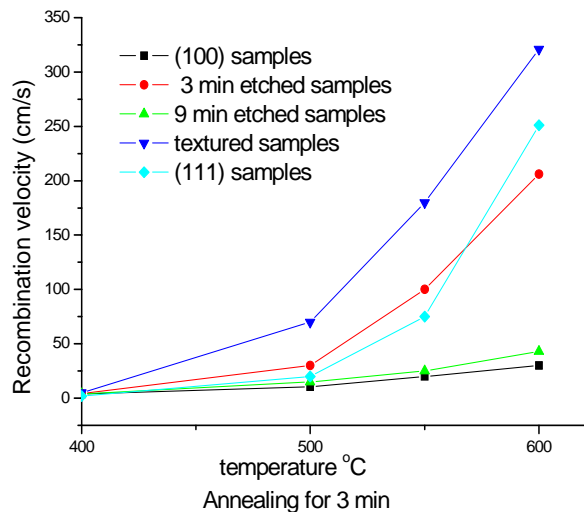


Fig 4: Surface recombination rate vs isochronal annealing

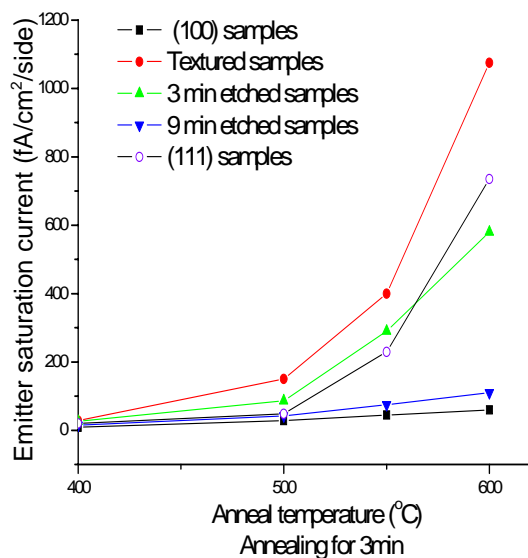


Fig 5: Emitter saturation current vs isochronal annealing

An important point to note is that while the overall surface area of the sample with inverted pyramids is obviously larger than that of the planar samples, the increase in surface area is not large (approximately 25%, since only less than a third of the surface is textured), and the area of (111) surface is actually less than that of the planar (111) samples. Thus, the behaviour of the textured samples cannot be explained by an increase in surface area. Another possible reason could be that the textured surfaces are more perfect (111) surfaces than those of (111)

planar wafers, which ordinarily have a tolerance on the surface orientation of +/- 0.5 degrees. The etching may introduce further changes at the atomic scale to these surfaces. However, it is surprising that even the textured wafers that were subsequently acid etched for 3 minutes display a behaviour similar to that of the (111) planar samples.

CONCLUSION

RTA and QSSPCD measurements were applied to test the thermal stability of different Si surface orientations. During isochronal and isothermal anneals, textured samples displayed the fastest depassivation rate. Surface orientations between textured surfaces and (100) surfaces showed a slower depassivation rate than the textured surface but a higher rate than the (100) surface. As the texture becomes more and more shallow, resulting in surfaces with orientations closer to (100), the depassivation rate gradually decreases and approaches that of (100) surfaces.

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