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Investigations on the correlation between surface texturing histogram and the spectral reflectance of (100) Crystalline Silicon Substrate textured using anisotropic etching

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ABSTRACT

Anisotropic etching of p-type Single crystalline (100) silicon substrate was optimized using KOH and IPA etchant combinations at constant temperature. Surface texturing histogram of the etched silicon substrates at different combinations were characterized using Zeta analysis, Scanning Electron Microscope and UV–vis spectral reflectance measurements. An increase in etchant ratio results in an increase in aspect ratio (height/base) and a decrease in the density of pyramid. Optimization of etchant ratio to 3:1 resulted in the presence of correlated pyramid distribution with an average aspect ratio of 0.44 and resulted in a lowest weighted reflectance of 10.76% for the spectral range from 300 nm to 1100 nm without anti-reflection coating.

1. Introduction

Photovoltaic output of a solar cell is directly proportional to the spectral input and the optical absorption coefficient ($\alpha(\lambda)$) of the semiconductor used [1]. Further, the optical absorption of the semiconductor is obtained from the refracted and diffracted light out of the total incident light [2,3]. Silicon is being utilized for the fabrication of low cost solar cells for power production, complementary metal-oxide-semiconductor (CMOS) image sensors, charge coupled devices (CCD), optoelectronic sensors, highly sensitive and high speed photo detectors, force sensors, three-axial tactile sensors, pressure sensors, IR sensors etc., [4–12]. In view of the above, it is reported that silicon wafers found reflecting highest values about 50–60% in the UV-A region (315 nm–400 nm), 60–70% in the UV-B region (280 nm–315 nm) and more than 70% in the UV-C region (200 nm–280 nm) depending upon the quality of the wafer [13,14]. Furthermore, a reflectance percentage between 20 and 40% in the absorption region of 400 nm–1100 nm have been reported depending upon the wafer quality, fabrication and surface process conditions [13–17]. Therefore, the optical reflectance of silicon wafers have been reduced by modifying the surface texturing by wet chemical etching, reactive ion etching, ultra-fast laser etching, electrochemical etching, electron beam lithography and mechanical grooving etc., along with antireflection coating [18–23]. As a consequence, some of the processes were reported lowering the reflection to ~2% in the visible as well as IR ranges resulting in the photovoltaic conversion efficiencies between 17 and 18% [24]. Furthermore, sophisticated etching techniques such as selective etching, patterned etching with pyramid and nano-patterning combined with antireflection coatings resulted in an improved light trapping as well as photovoltaic efficiencies up to 19–20% [25]. To the best, Honey-comb surface structure with buried contact combined with MgF + ZnS antireflection coating (ARC) was reported with a highest efficiency of 25 ± 0.5% after spectral correction [26]. Application of surface texturing to silicon substrate removes the portion of material selectively at the surface creating either upright or inverted pyramidal structure based on the texturization procedure adopted. As a consequence, the density of material gets reduced at the surface resulting in a complex dielectric contrast at the surface, which favors for the wavelength dependent reduction of surface reflection [27]. In addition, it is reported that the presence of pyramidal structure at the surface favors to: (i) multiple reflection between the adjacent facets of the pyramids ensuring more than one chance for light to penetrate in to the surface, (ii) provide wide oblique angle due to the presence of inclined facets and also (iii) establishes multiple internal reflection for the transmit-

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ted low energy photons paving way for absorption [28]. The details of light trapping through the upright pyramidal structure is being discussed in detail by Deinega et al., narrating the essential requirement of optical correlation between the pyramids [29]. Kexun chen et al., elaborated the optimum height distribution of upright random pyramids for obtaining less reflectance [30]. The requirement of pyramid size, effect of pyramid height and the impact of structural homogeneity on the reflectance losses have been discussed by various authors and reported [31–33].

Besides, it is found from the reports that texturization resulting in an inhomogeneous pyramid distribution, which in turn resulting in different cumulative optical reflection characteristics based on the composition of in-homogeneities, which is case specific. Moreover, the reported optimized surface texturing for the lowest reflectance fails to result in minimum reflection in the UV spectral region on silicon [26]. In this regard, we believe that an in-depth analysis of texturing histogram with respect to the texturization conditions as well as the optical reflectance is expected to result in an achievement of optimized etching conditions for achieving lowest reflectance in the entire spectral absorption region of silicon. Therefore selection of proper etchant or etchant composition is an essential requirement for obtaining uniform pyramidal distribution as well as low reflectance [34]. In this regard, various etchants such as Ethylenediaminepyrocatechol (EDP), hydrazine, NaOH, Na_2CO_3, Na_3PO_4, Na_2SiO_3, KOH, and TMAH have been tried to obtain surface texturing with an expectation of uniform distribution of pyramidal structures [35–40]. Among them, KOH along with IPA is reported having predominant anisotropy in etch rates along different orientation such as the demonstrated faster etch rate along (100) plane (at least 10 times faster) than (111) planes irrespective of its solution concentration [41]. This preferential etching leads to the formation of very sharp pyramidal structures with an opportunity to alter the pyramidal density by altering the self-organized IPA monolayer as reported [42].

In this work, efforts are made to modify the etching patterns by varying the KOH concentration with respect to IPA and analyze the histogram of the textured surfaces and its optical reflectance. It is found that the pyramidal density varies with KOH concentration resulting in corresponding changes in their aspect ratio as well as optical reflectance. An optimized etching condition was characterized for a lowest reflectance in the entire spectral absorption range of silicon. Details are reported.

2. Experimental

Solar grade p-type single crystalline silicon wafer of (100) orientation was surface cleaned using the standard procedure of H_2SO_4 mixed with H_2O_2 (2:1) at 85 °C followed by HCl mixed with $H_2O_2 + H_2O$ (HPM) in the ratio of 1:2:5 at 80 °C [43]. Cleaned wafers were further rinsed in 10% HCl followed by 10% HF solution and DI water to remove the native oxides if any before proceeding for etching. Etching was carried out using solution comprises of etchant (KOH), the surfactant (IPA) and de-ionized water (DIW) in an experimental setup designed to carry out etching with controlled temperature using oil bath and with a reflux condenser fixed on top of the etchant flask to maintain etchant concentration. Stirring was used to keep homogenous etchant concentration throughout the bath.

According to Arrhenius relation, the temperature corresponding to the activation energy of the electron for an etching in silicon planes fall around 60 °C to 85 °C [44]. Hence, optimization of time and temperature was carried out using post measurement of reflectance spectrum after etching and noted as 80 °C for 1 h resulted in least reflectance. Further, an optimization of etchant to surfactant ratio was carried out by varying the KOH concentration with respect to one molar IPA concentration.

Textured wafers were further characterized using Scanning Electron Microscope (SEM) using HITACHI S-3400N, ZETA analysis using ZETA 20 3D optical profiler and UV–vis reflectance measurements using SHIMADZU UV-3600 plus spectrophotometer.

3. Result and discussion

Etching of crystalline silicon wafer using aqueous KOH starts with: 1). dissociation of KOH in H_2O and generation of K^+ as well as OH^- ions, 2). The continued back bond attack of the OH^- ions by generating H-terminated silicon surface, 3). followed by reaction of OH^- ions with H-terminated silicon converting in to OH terminated surface and 4). Finally the surface silicon is removed either as $Si(OH)_6$ or K_2SiO_3 as reported [45,46]. In addition, IPA acts as surfactant to open up the surface sites by transporting the chemical products as stated earlier [47]. Therefore, the etch rate is highly depends on the presence of OH^- ion and H_2O concentration and its accessibility to the surface sites cleared by IPA [48]. Considering the facts, etching was performed using different molar concentrations of KOH with respect to IPA stating from 1.5 M to 9 M and characterized using Zeta 3D surface profiler analysis as well as SEM analysis to identify the optimum etching condition to obtain lowest reflectance. Fig. 1(a–e) shows the etchant ratio versus the plot of pyramid distribution in terms of base (i) & height (ii) obtained by Zeta 3D surface profiler analysis and its corresponding SEM images in (iii). It is worth noting that the distribution of both the base and height for 9 M KOH concentration shown in Fig. 1a (i,ii) is random with average sizes of 2.806 μm and 3.652 μm respectively. The reduction in KOH molar concentration resulted in more numbers of pyramids with narrowing base distribution as shown in figures (Fig. 1a (i,ii), b(i,ii)& c(i,ii)), which is different from the morphology and distribution reported for similar KOH concentrations in the reports [49]. At 3 M concentration, the base and height distributions were recorded as 2.154 μm and 0.9615 μm respectively as shown in Fig. 1d (i,ii). Further, an unclear pyramid structure of pronounced hillock morphology with 2.321 μm base and 0.8673 μm height distribution was recorded for 1.5 M KOH concentration as shown in Fig. 1e (i,ii). In view of the above, generation and appearance of hillock morphology due to modified etch rates contributed by change in KOH/IPA concentration is reported describing that an increase in IPA concentration upon reduction in the ratio promotes micro masking due to the self-assembly of IPA molecules along with water molecules [49,50]. Whereas, present observation reveals that the reduction in KOH concentration alters the etching pattern resulting in an increase in the density of pyramids with clear morphology up to 3 M and that changes in to pronounced hillocks morphology below 3 M (Fig. 1, all SEM images). This observation of change in morphology to hillock structure and the increase in number of hillocks with decrease in KOH concentration leading to an increase in IPA ratio in the etching solution are analogous to the reports of similar trend observed [51]. The observed continuous decrease in base distribution (Fig. 1a (i) to d (i)) as well as an increase in pyramid density evidences that at lower concentration of KOH, the etching is favored with localized etching may be due to the facts of IPA masking as well as the lower concentration of OH^- ions and its reduced impact on the etching chemistry as described earlier [52].

Furthermore, the etchant ratio (KOH/IPA) versus aspect ratio (height/base) of the pyramids were plotted and presented in Fig. 2 with the insets of corresponding SEM images. It shows that an increase in KOH molar ratio in turn increases the aspect ratio stating that the height of the pyramid increases. Analogous observation of an increase in pyramid dimensions with an increase in KOH concen-