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EFFICIENT SURFACE PASSIVATION OF N-TYPE BLACK SILICON

Surface recombination losses significantly reduce the efficiency of black silicon (b-Si) for solar cell applications. Surface passivation using suitable dielectric films can minimize these losses. This paper reports the investigation on the passivation properties of the hafnium dioxide (HfO_2) film deposited on n-type b-Si surface via the atomic layer deposition method. It is shown that in addition to efficient passivation, HfO_2 film reduces the reflectance of the b-Si surface in the wide spectral range.

Keywords: black silicon, solar cell, passivation, reflection, atomic layer deposition, hafnium dioxide.

Introduction. Black silicon (b-Si) or silicon grass is a needle-like surface where needles are made of single-crystal Si and have a height 0.3…10 μm and diameter 0.05 …1.0 μm. These surfaces can be fabricated by the reactive ion etching (RIE) method, which exhibits some distinct advantages. First, it is a reliable and reproducible, yet self-organized process that does not necessitate any additionally applied mask. Second, the method leaves the crystallographic intact nanostructure surfaces free of chemical contaminations, in contrast, e.g., to structures obtained by wet etching. Third, it cannot only be applied to poly- and monocrystalline wafers, but also to amorphous or crystalline Si thin films.

The unusual optical characteristics make b-Si interesting for solar cell applications as antireflection surfaces [1-4]. This is due to the needles of b-Si that would multi-reflect the incident light and thus reduce the reflectance, leading to an enhancement of absorptance.

Although an especially low surface reflection ratio has been achieved by b-Si, the final energy-conversion efficiency of solar cells is not satisfied at present. The main problems are as follows. The b-Si solar cells suffer from increased surface recombination rates due to the larger surface area resulting in poor spectral response especially at short wavelengths. In addition, the huge internal surface of the needles tends to be progressively oxidized or contaminated by impurities when in contact with air. The only way to overcome these drawbacks is the effective passivation and stabilization of the b-Si surface [5, 6].

Nowadays, some works demonstrate that excellent passivation of b-Si surfaces can be achieved using aluminum oxide (Al_2O_3) films grown via the atomic layer deposition (ALD) method [7-10]. The general advantage of the ALD method is that it can be used for a large area deposition and processed at a low temperature. With ALD, good film quality, accurate thickness control and conformality are achieved. In particular, ALD Al_2O_3-passivated b-Si has been used as a material in record breaking solar cells reaching efficiencies above 22.1% [10].

However, an Al_2O_3 passivation film has negative fixed charges, which result in an inversion layer on the n-type Si surface, causing short-circuit current loss due to the parasitic shunting between this inversion layer and metal contact. Therefore, the passivation quality provided by Al_2O_3 on n-type Si surfaces is limited. The dual layer stacks of SiO_2/Al_2O_3 and Al_2O_3/TiO_2 prepared by ALD have both been demonstrated to passivate the n-type b-Si surfaces [11, 12] but a dielectric stack requires separate reactors in production to account for different process temperatures and avoid the risk of cross contamination.

This paper demonstrates the use of ALD hafnium dioxide (HfO_2) films as a novel candidate for n-type b-Si surface passivation. HfO_2 films have positive fixed charges and this makes it very suitable for passivation of n-type Si wafers [13]. ALD HfO_2 was also chosen for investigation due to its higher dielectric constant (k~25) than that of the Al_2O_3 film (k~9), a large energy band gap (~5.68 *eV*) and thermodynamic stability in contact with Si surface [14, 15].

Experimental details. The experiments were performed on double-side polished Czochralski-grown phosphorus-doped Si wafers (100) oriented and of resistivity 3.0 *Ω.cm*. The wafer thickness was 440 μm and the oxygen level was 8.0 *ppma*.

The b-Si layers on the front surfaces of Si wafers were fabricated by the RIE method in a gas mixture of sulfur hexafluoride (SF_6) and O_2 by the multi-cathode RIE chamber (Fig. 1). The mixture SF_6/O_2 is non-toxic and easy to handle. The process pressure was 55 *mTorr* and the gas flow rates were 75 cm^3/min and 40 cm^3/min for SF_6 and O_2, respectively. The samples were placed on the water-cooled (23°*C*) bottom electrode that was powered by a 13.56 *MHz* RF generator. The etch durations were kept constant at 10 *min*.

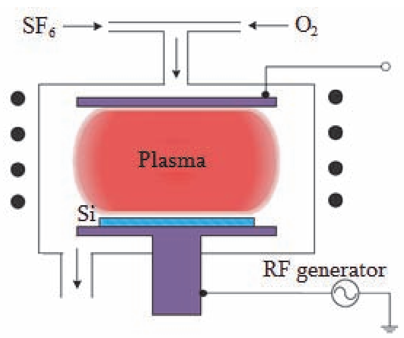


Fig. 1. Schematic view of the RIE chamber

After the RIE process, all samples were previously cleaned using the following sequence of steps: 1) boiling in acetone to remove the presumable surface organic contamination; 2) boiling in the NH_3:H_2O_2:H_2O (1:1:7) solution; 3) dipping into the 5% HF solution for 30 *s*. Rinsing in deionized water was performed after each step.

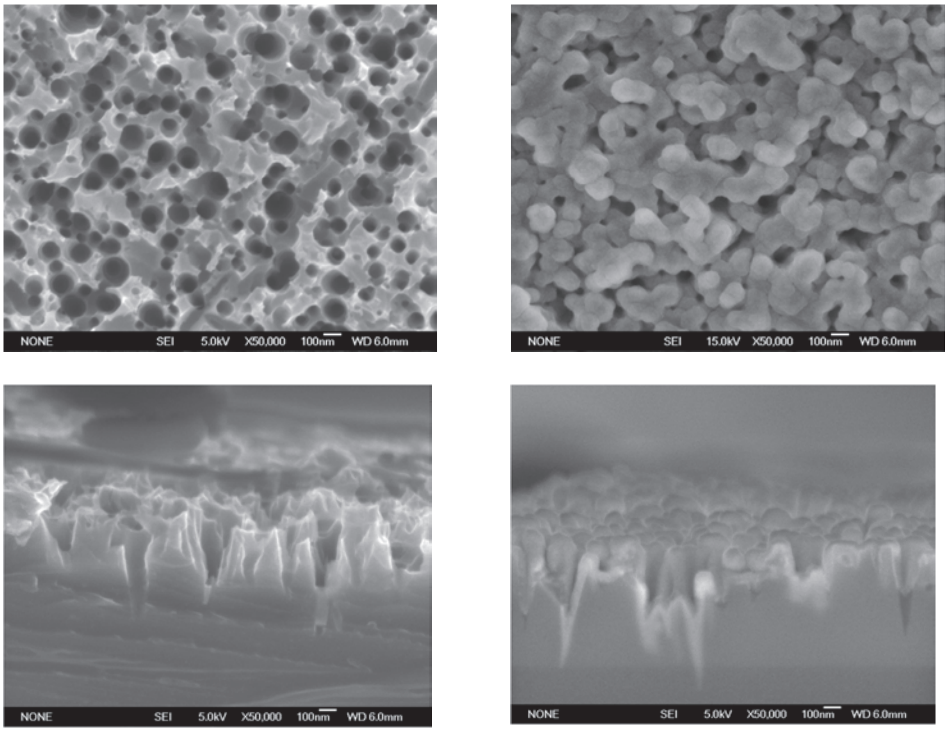
The HfO_2 films with a thickness of 40 *nm* were deposited on b-Si in a hot-wall Picosun Oy Sunale R-200 ALD reactor (Finland) at an evacuation to about 1 *mbar*. Pure nitrogen (99.999*%*) was used as a carrier gas and for purging the reactor after each reagent pulse. The well-known TEMAH (tetrakisethylmethylamido hafnium (IV), $Hf[N(CH_3)(C_2H_5)]_4$) + H_2O precursor system was used [15]. TEMAH was delivered into the reactor from the heated source at 100°*C*. The wafer temperature was 250°*C*. The passivation films were activated by post-deposition in-situ annealing in N_2 ambient for 50 *min* at 440 *ºC*. The samples were taken out from the reactor after cooling at room temperature. The thickness and refractive index of as-deposited and annealed samples were measured by ellipsometry. Unetched planar wafers (without b-Si) were coated as reference samples.

The cross-section and top-view morphology of the b-Si was observed by a scanning electron microscope (SEM). The optical reflectance of the b-Si surfaces was detected using a spectrophotometer T70 UV-VIS with an integrating sphere. The charge carrier lifetime was characterized using the photoconductance method in the transient mode (WTC-120 Sinton Instruments).

Results and discussion. Cross-section and top-view SEM images of the b-Si surfaces with and without an ALD HfO_2 film are shown in Fig. 2.

The morphology of the b-Si surface without a passivation film (Fig. 2,a) consists of slightly rounded needles with an average height of 400 *nm* and average spacing of 150 *nm*. In Fig. 2,b, the HfO_2 film can be distinguished from the cross-section as a lighter, narrow layer on top of the needles. It can be seen that the needles have been coated perfectly conformal with a HfO_2 passivation film, no blistering was observed after annealing on OH-terminated surfaces. Small changes in the b-Si nanostructure height and shape can be seen, i.e. the needles become shorter and denser. This can be attributed partly to the annealing of the films at 440 *ºC*.

Thus, the ALD HfO_2 films precisely reproduce the morphology of the b-Si surface without any voids or inclusions. As a result, a good chemical passivation can be obtained.

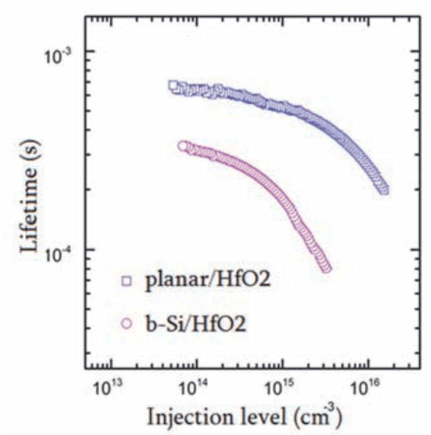


a) b)

Fig. 2. SEM images of the b-Si surfaces with (b) and without (a) ALD HfO_2 film. The upper and the lower row display top-view and cross-section images, respectively.

Fig. 3 shows the minority carrier lifetimes as a function of injection level in planar Si wafer and b-Si surface coated by a ALD HfO_2 film. These two samples were fabricated using the identical ALD process.

The minority carrier lifetime is a relevant parameter of merit to estimate the surface recombination and surface damage. As can be seen from Fig. 3, the lifetime difference between the planar Si wafer and b-Si surface coated by an ALD HfO_2 film is not significant and the measured lifetimes are in the $10^{-3}\ldots10^{-4}$ *s* range. Therefore, despite the high surface area of b-Si and the potential surface damage induced by the RIE process, the passivation quality of HfO_2 on the b-Si surface is comparable to its passivation quality on the planar Si wafer. The improved surface passivation could be attributed to a reduction in the electrically active defect density at the Si/HfO_2 interface. Hydrogen from the HfO_2 bulk could diffuse to the interfacial region and provide the chemical passivation of the dangling bonds, reducing the defect related recombination rate [13]. Note also that the obtained carrier lifetimes by ALD HfO_2 films are comparable to that by ALD Al_2O_3 films [7-9].



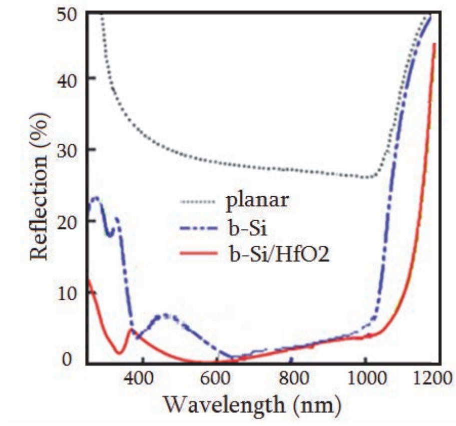


Fig. 3. Minority carrier lifetimes as a function of injection level in the planar Si wafer and the b-Si surface coated by ALD HfO_2 films

Fig. 4. Reflectance of the planar Si wafer and the b-Si surface with and without an HfO2 film

Reflectivity measurements of three types of surfaces (planar Si wafer, b-Si surface with and without a HfO_2 film) are given in Fig. 4. As it is seen, the b-Si surface achieves a reflectance below 10% in the whole visible spectrum, as well as in the near UV and near IR regions. As a comparison, the reflectance of the planar Si wafer varies between 30 and 50% in the same wavelength range. By applying the ALD HfO_2 films on the b-Si surfaces, the reflectivity was decreased significantly to a minimum of 0.2…0.4% at around 500 *nm*. At the 700…1000 *nm* region of wavelength, the reflectance for the b-Si surface with and without a HfO_2 film is similar; while at higher wavelength, the reflectance for the b-Si surface with a HfO_2 film is a little lower than the surface without a HfO_2 film. Thus, in addition to the surface passivation, the ALD HfO_2 film further reduces the reflectance on the whole spectral range relevant for the solar cell operation. This is in agreement with the recent results, when the b-Si surface is coated with ALD Al_2O_3 films [7-9].

Conclusion. The increase in the surface recombination has always hindered the application of b-Si in solar cells. Our invetigations show that the ALD HfO_2 film can solve this problem by providing completely conformal coating and excellent passivation on n-type b-Si surfaces. Besides, the ALD HfO_2 film reduces the reflectance of the b-Si surface on the whole spectral range relevant for the solar cell operation. The excellent surface passivation and low reflectance results prove the potential of using the combination of the b-Si surface and the ALD HfO_2 film in different photovoltaic devices. In particular, their application in the spectral selective double barrier n-type Si photodetectors is very actual [16].

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N-ՏԻՊԻ ՍԵՎ ՍԻԼԻՑԻՈՒՄԻ ՄԱԿԵՐԵՎՈՒՅԹԻ ԱՐԴՅՈՒՆԱՎԵՏ ՊԱՍՍԻՎԱՑՈՒՄԸ

Մակերևութային վերամիավորման կորուստները զգալիորեն փոքրացնում են սև սիլիցիումի (b-Si) արդյունավետությունը արևային էլեմենտներում կիրառելու համար: Այդ կորուստները կարելի է նվազեցնել՝ մակերևույթը պասսիվացնելով որոշակի մեկուսիչ թաղանթներով: Հետազոտվել են n-տիպի b-Si-ի մակերևույթին ատոմաշերտային նստեցման մեթոդով ստացված հաֆնիումի երկօքսիդի (HfO_2) թաղանթի պասսիվացման հատկությունները: Ցույց է տրվել, որ HfO_2 թաղանթը, բացի արդյունավետ պասսիվացումից, նվազեցնում է նաև b-Si-ի մակերևույթի անդրադարձումը սպեկտրային լայն տիրույթում:

Առանցքային բառեր. սև սիլիցիում, արևային էլեմենտ, պասսիվացում, անդրադարձում, ատոմաշերտային նստեցում, հաֆնիումի երկօքսիդ:

Г.Е. АЙВАЗЯН, С.Х. ХУДАВЕРДЯН, М.С. ЛЕБЕДЕВ, А.В. СЕМЧЕНКО

ЭФФЕКТИВНАЯ ПАССИВАЦИЯ ПОВЕРХНОСТИ ЧЕРНОГО КРЕМНИЯ N-ТИПА

Потери, обусловленные поверхностной рекомбинацией, значительно снижают эффективность черного кремния (b-Si) для применения в солнечных элементах. Пассивация поверхности с использованием определенных диэлектрических пленок может минимизировать эти потери. Исследованы пассивирующие свойства пленки диоксида гафния (HfO_2), нанесенной на поверхность b-Si n-типа методом атомно-слоевого осаждения. Показано, что, помимо эффективной пассивации, пленка HfO_2 снижает отражение поверхности b-Si в широком спектральном диапазоне.

Ключевые слова: черный кремний, солнечный элемент, пассивация, отражение, атомно-слоевое осаждение, диоксид гафния.