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MACROPOROUS TEXTURING OF MULTICRYSTALLINE SILICON FOR SOLAR CELLS

MAKROPOROWATA TEKSTURYZACJA KRZEMU MULTIKRYSTALICZNEGO DLA OGNIW SŁONECZNCYH

It was shown that palladium deposited by immersion of Si wafers in $PdCl_2$ solution can be used as a catalyst for macro-porous formation by chemical etching of silicon. The light reflectance of silicon surface with macro-porous layer was considerably reduced in the whole region of 400-1000 nm. The lowest effective reflectivity of mc-Si wafers with a new kind of texturization was equal to 4.2%. Presented method of texturization is very simple and can be used to improve the efficiency of multi-crystalline silicon solar cells.
Keywords: texturization, metal-assisted chemical etching, macroporous silicon

Zostało pokazane, że pallad osadzany na powierzchni krzemu z roztworu $PdCl_2$ może być użyty w roli katalizatora w procesie wytwarzania krzemu makro-porowatego metodą trawienia chemicznego. Uzyskano znaczne obniżenie odbicia światła od powierzchni krzemu w całym zakresie długości fal 400-1000 nm. Najmniejsza wartość efektywnego współczynnika odbicia z nowym typem tekstury powierzchni wynosiła 4.2%. Przedstawiona metoda teksturyzacji jest bardzo prosta i może być wykorzystana do poprawy sprawności produkowanych fotoogniw z krzemu multi-krystalicznego.

1. Introduction

The polycrystalline silicon with a big, columnar grains, so-called multi-crystalline silicon (mc-Si), is in the PV (photovoltaics) field one of the most important basic materials used for solar cells manufacturing. As-cut mc-Si wafers are used as start materials for the solar cells production. The process sequences of cells manufacturing is consisted of several technological processes like: texturization, junction formation, anti-reflection coating deposition and metallization. The word "texture" is used here, as in PV community, as a description of surface topography. The process of texturing of silicon surface is used in order to reduce the optical losses caused by surface reflectance. For <100> oriented surface of single-crystal silicon the method of texturing is very simple and effective. It is an anisotropic etching in KOH solution which results in the surface covered by a microscopic random pyramids about several micrometers in size. However, in the case of multi-crystalline wafers this method is not very effective because the grains have different crystallographic orientations. Therefore, several other methods of texturization are developed. Presently, the acidic isotropic etching is becoming a standard method for screen-printed solar cell. The other kinds of texturization which are very promising are based on submicron texturization. The size of pores is less than the wavelength of light. Therefore, the microstructure can be modeled by the effective medium theory as a mixture of air and silicon with a gradient change of composition and graded optical constants. It was shown that this type of texturization has low and uniform reflectance in the all range from 300-1000 nm. One of the method for producing that kind of microstructure is reactive ion – etching which allows to receive black silicon with needle-like structure.

The other method which is developed by some groups is metal-assisted chemical etching. In this method a thin metallic film like Pd, Au or Al is deposited on the silicon before chemical etching in solution composed of hydrofluoric acid and oxidizing agent. Koynov et al. [1] showed that gold in the form of nano-clusters deposited by the thermal evaporation serves as catalyst for porous silicon etching. After chemical etching in an $HF:H_2O_2:H_2O$ solution the black silicon with reflectance below 5% in the range 350-1000 nm was obtained. Sim-

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ilar method was described by Hadjersi [2] who used the thin film of Pd deposited by evaporation. The reflectance was about 5.6% in the 250-1000 nm range.

The aim of this work was to test a new method of metal-assisted porous silicon formation. In this method the catalyst Pd is deposited by immersion in the solution in the place of evaporated thin film of metal.

2. Experiment

The starting material was p-type polished monocrystalline silicon (Cz-Si) wafers of resistivity 6-8 Ωcm and as-cut multi-crystalline silicon wafers of resistivity 0.5-2.0 Ωcm. All wafers were first degreased using an isopropyl alcohol. The mc-Si wafers were additionally etched in KOH in order to removing saw damaged of surfaces. In the next step all the wafers were put into diluted hydrofluoric acid (HF) for 2 min which makes the surface hydrophobic. In order to obtain the "black silicon" the wafers were first immersed for several minutes in modified solution of $PdCl_2$ used for electroless deposition of metals on nonconductors. After this operation the surface of silicon was changed from a hydrophobic into hydrophilic. The chemical analysis of Si surface by X-Ray photoelectron Spectroscopy (XPS) indicates that the surface is covered by Pd atoms. Figure 1 shows the XPS spectrum of Si surface with two peaks of Pd(3d). In the next step, the wafers were etched in the solution $HF:H_2O_2:H_2O$ used by Koynov et al. [1]. After some minutes the surfaces of the wafers became dark. It was observed that the solution does not etch the surfaces of Si wafer without immersing in the $PdCl_2$ solution which means that deposited palladium is a catalyst of the chemical etching. If the samples of "black Si" are put into 2 mol KOH solution the gas bubbling occurs for about two minutes which gives an evidence that the top layer has a nano-porous structure. This nano-porous Si is not profitable for the PV application due to high recombination of charge carriers. In order to remove it and to modify the morphology of the surface as well, the surfaces were etched in 2 ml HF (40%):98 ml HNO_3 (65%) [4]. It is know that etching of Si by this solution is isotropic for both *n* and *p* type Si and rate of etching is very low (~0.25 μm/min). Therefore, it can be used for modification of topography of Si without destroying the texturizaton. The total reflectivity of samples was measured using a Perkin-Elmer Lambda 19 spectrophotometer equipped with an integrating sphere. In order to evaluate qualitatively the reflectance regarding application for solar cells, the effective reflectivity R_E calculated by integrating reflectance under AM1.5 standard solar illumination for the 400-1000 nm wavelength range [3]. The morphology of such surfaces was investigated by Scanning Electron Microscopy.

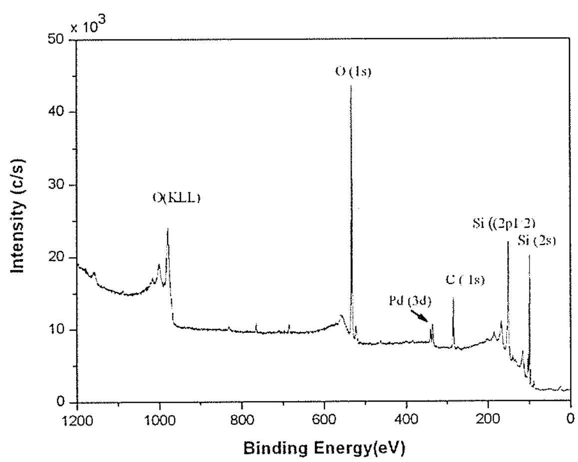

Fig. 1. XPS spectrum of Si surface covered by palladium atoms

3. Results and discussion

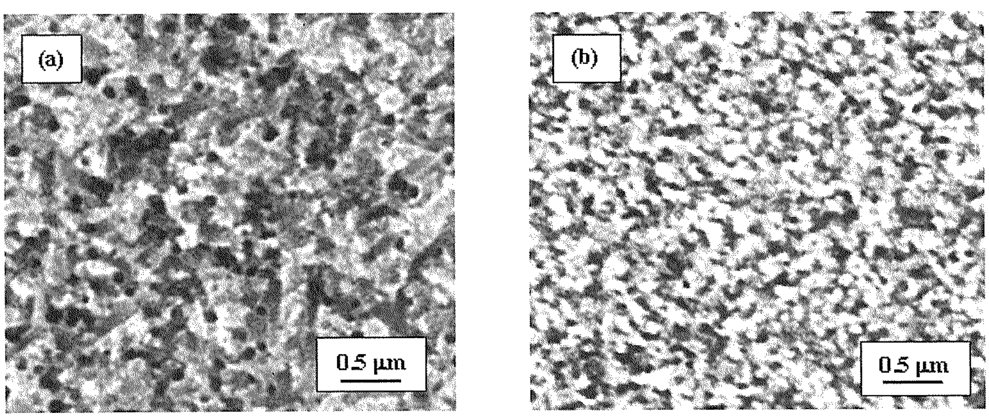

Fig. 2. SEM image of Si(111) after macro-porous silicon formation and additional chemical etching in 2 ml HF:98 ml HNO_3 solution for 1 min (a) and 2 min (b)

3.1. Morphology

Figure 2 shows a morphology of two samples of Cz-Si with the macro-porous layers. The time of additional etching in 2 HF:98 HNO_3 was 1 min (a) and 2 min (b). It is shown that surface is rough with sub-micrometer holes. The additional etching during 2 minutes improves the quality of the surface which becomes more homogenous in comparison with surface etched during 1 min.

3.2. Reflectivity

Figure 3 shows that total reflectance of the multi-crystalline Si (a) and monocrystalline silicon (Cz-Si) (b) surfaces with macro-porous silicon layers is lower compared to KOH textured surfaces. The reflectance of mc-Si sample without additional etching in acidic solution (Fig. 3a) is less than 5% and is nearly constant over whole range of wavelength (400-1000 nm). The lowest effective reflectivity R_E equal to 4.2% was obtained for mc-Si with macro-porous layer modified by 2 min etching. This value is lower compared to value of R_E for mc-Si wafers KOH textured (R_E = 20.5%). The effective reflectivit was reduced also for monocrystalline silicon (Cz-Si).

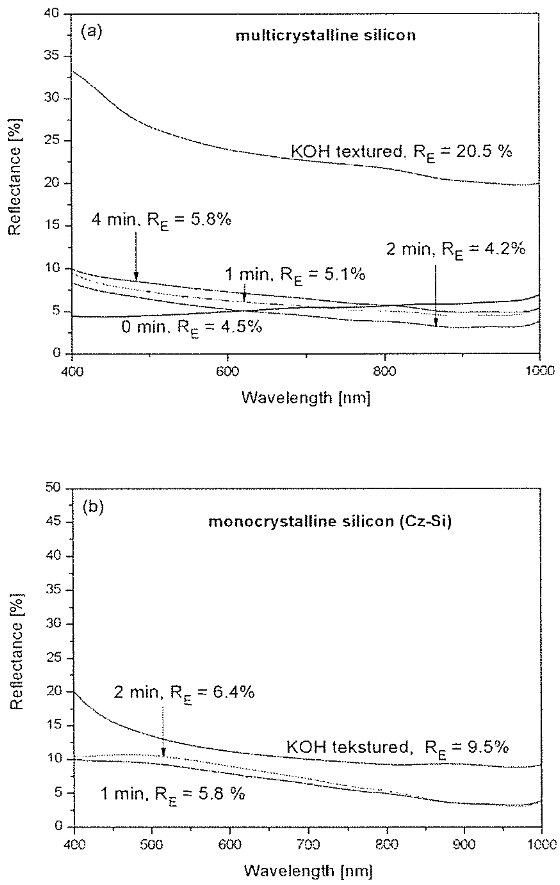

Fig. 3. Total reflectance of silicon with macro-porous layer after modification by chemical etching (a) for mc-Si wafers, (b) for polished single crystal silicon wafers, in comparison with standard KOH textured wafers. The effective reflectivity (R_E) is shown for each curve

4. Conclusion

The thin film of palladium deposited by immersion of wafers into $PdCl_2$ solution can be used for macro-porous silicon formation by metal – assisted chemical etching of silicon. It was shown that reflectance of Si wafers was reduced in the whole region of 400-1000 nm. The lowest effective reflectivity of mc-Si wafers with new kind texturization is equal to 4.2%. This value is considerably lower compared to mc-Si textured by standard KOH. The presented method of texturization is very simple and shows big potential for improving the efficiency of mc-Si solar cells.

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