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ScienceDirect

Energy Procedia 124 (2017) 435–440

Energy Procedia

www.elsevier.com/locate/procedia

7th International Conference on Silicon Photovoltaics, SiliconPV 2017

Introducing pinhole magnification by selective etching: application to poly-Si on ultra-thin silicon oxide films

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Abstract

Carrier selective junctions formed by polycrystalline silicon (poly-Si) on ultra-thin silicon oxide films are currently in the spotlight of silicon photovoltaics. We develop a simple method using selective etching and conventional optical microscopy to determine the pinhole density in interfacial oxide films of poly-Si on oxide (POLO)-junctions with excellent electrical properties. We characterize the selective etching of poly-Si versus ultra-thin silicon oxide. We use test structures with deliberately patterned openings and 3 nm thin oxide films to check the feasibility of magnification by undercutting the interfacial oxide. With the successful proof of our concept we introduce a new method to access the density of nanometer-size pinholes in POLO-junctions with excellent passivation properties.

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Peer review by the scientific conference committee of SiliconPV 2017 under responsibility of PSE AG.

Keywords: polysilicon; carrier selective contacts; pinholes; Tetramethylammonium hydroxide (TMAH)

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Peer review by the scientific conference committee of SiliconPV 2017 under responsibility of PSE AG.
10.1016/j.egypro.2017.09.270

1. Introduction

Carrier selective junctions formed by polycrystalline silicon-rich layers on ultra-thin silicon oxide films are currently in the spotlight of silicon photovoltaics research. Remarkable junction passivation and low specific contact resistances [1,2] have enabled conversion efficiencies of 25.3% with the TOPCon-approach for one carrier polarity [3] and 25.0% applying poly-Si on oxide (POLO)-junctions for both carrier polarities [4].

A plethora of models has been developed to explain the basic principle behind the carrier selectivity of POLO-junctions since their first application to silicon bipolar junction transistors decades ago [5,6]. The break-up of the interfacial oxide film under annealing has been identified as a crucial process step to achieve high quality junctions [7,8]. On the one hand the formation of holes in the oxide film has been regarded as detrimental to the electrical junction properties [9]. On the other hand localized carrier transport through pinholes in the interfacial oxide has been discussed as a key mechanism beside direct tunneling [10,11]. So, the determination of size and density of pinholes in POLO-junctions with good electrical properties would be an important step towards a more accurate description of the current transport mechanism and predictive modelling of the junction formation process. Practically, optimization strategies might be deduced from the knowledge of the microstructural properties and their dependency on process parameters.

Unfortunately, finding nanometer-size pinholes at densities below 10^9 cm^{-2}, as expected for a POLO-junction with good electrical properties [10], is very challenging. In a recent transmission electron microscopy (TEM) study it was possible to identify about 5 nm small regions of direct contact between the crystalline silicon and the poly-Si layer in POLO-junctions with excellent passivation properties [12]. TEM only allows an approximate estimation of the density of these regions [12]. Clearly, a less uncertain method to measure the pinhole density is required. One approach could be conductive atomic force microscopy [13]. One limitation of this method is the lateral conductivity of the poly-Si films, which has to be small in order to enable the required resolution. Another approach, which circumvents the latter constraint, is presented here. We combine selective etching and simple optical microscopy (OM). First, the poly-Si has to be removed without harming the ultra-thin silicon oxide film underneath to make the pinholes accessible by OM. This requires a highly selective etching process. We use tetramethylammonium hydroxide (TMAH) which is frequently used in microelectronics and micromechanics as an anisotropic etchant for silicon and known for high selectivity to silicon oxide. Secondly, nanometer-size pinholes have to be magnified to the micrometer range for OM detection. We exploit the fact that openings in the oxide film result in undercutting for overetching conditions. This can yield etch pits large enough to be visible in OM. The feasibility of this second step is demonstrated in a proof of principle experiment using lithographically patterned openings in a less than 3 nm thin silicon oxide film.

2. Experimental

Two sets of samples were prepared for optimizing the selectivity between silicon and silicon oxide for etching with TMAH solution. On a first set of silicon wafers, a dry thermal oxide with a thickness above 50 nm was grown at 1000 °C. These wafers were used to determine the etch rates of TMAH for SiO_2. A second set of wafers was prepared to measure the TMAH etch rate for poly-Si films. Therefore, etch stop layers were applied (SiN_x or SiO_2), whose only purpose is to prevent etching into the silicon wafer after complete removal of the poly-Si layers. The latter were prepared by low pressure chemical vapor deposition (LPCVD) with thicknesses of 100 - 220 nm. Besides intrinsic poly-Si, phosphorous and boron doped poly-Si layers were produced *in situ* (n, p^+) or using ion implantation (p). The dopant concentrations are above $6 \cdot 10^{19}$ atoms/cm^3 for the *in situ* doped n poly-Si layers, $3 \cdot 10^{19}$ atoms/cm^3 for the ion implanted p poly-Si layers and above the solid solubility limit for the *in situ* boron doped p^+ polysilicon layers.

The etch rates of TMAH for poly-Si and SiO_2 were determined for different temperatures (70 °C, 80 °C and 90 °C) and concentrations (5%, 10%, 15% and 25%). All wafers were separated into several pieces and the thicknesses of silicon oxide and poly-Si were determined by spectroscopic ellipsometry. After etching in TMAH, the thicknesses were measured again, to determine the etching rate within certain time intervals.

To prove that the selectivity is sufficiently high for undercutting and thus magnifying openings in the oxide, a 10 nm thick thermal oxide on Si wafers was lithographically patterned to produce holes with edge lengths of 1 µm

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