Thin Solid Films 612 (2016) 243–249

Contents lists available at ScienceDirect

Thin Solid Films

journal homepage: www.elsevier.com/locate/tsf

Damage-free laser patterning of silicon nitride on textured crystalline silicon using an amorphous silicon etch mask for Ni/Cu plated silicon solar cells

Mark S. Bailly *, Joseph Karas, Harsh Jain, William J. Dauksher, Stuart Bowden

[a] Department of Electrical, Computer, and Energy Engineering, Arizona State University, Tempe, AZ 85284-1808, USA
[b] Solar Power Lab, Arizona State University, 7700 S River Parkway, 85284-1808 Tempe, USA

ARTICLE INFO

Article history:
Received 31 March 2016
Received in revised form 31 May 2016
Accepted 6 June 2016
Available online 7 June 2016

Keywords:
Laser patterning
Silicon nitride
Plating
Textured silicon
Sacrificial layer
Femtosecond laser

ABSTRACT

We investigate the optimization of laser ablation with a femtosecond laser for direct and indirect removal of SiN_x on alkaline textured c-Si. Our proposed resist-free indirect removal process uses an a-Si:H etch mask and is demonstrated to have a drastically improved surface quality of the laser processed areas when compared to our direct removal process. Scanning electron microscope images of ablated sites show the existence of substantial surface defects for the standard direct removal process, and the reduction of those defects with our proposed process. Opening of SiN_x and SiO_x passivating layers with laser ablation is a promising alternative to the standard screen print and fire process for making contact to Si solar cells. The potential for small contacts from laser openings of dielectrics coupled with the selective deposition of metal from light induced plating allows for high-aspect-ratio metal contacts for front grid metallization. The minimization of defects generated in this process would serve to enhance the performance of the device and provides the motivation for our work.

Published by Elsevier B.V.

1. Introduction

Laser patterning of thin films such as Silicon Nitride (SiN_x), Silicon Oxide (SiO_x), and hydrogenated amorphous silicon (a-Si:H) is desirable for Silicon (Si) solar cell production; it allows for patterning similar to that which is achieved with photolithography at a fraction of the cost and may be used for processes such as contact patterning and selective doping [1–6]. However, a major challenge for a laser ablation process is the c-Si damage typically induced by the laser. While 'low damage' laser patterning is trivial on smooth surfaces, performing such patterning on surfaces textured by the standard mono-crystalline Si alkaline etch process proves more difficult [7–9].

Knorz et al. demonstrated an order of magnitude variation in laser intensity across pyramidal structures 5–10 μm in size [7]. These variations in laser pulse intensity are detrimental towards the ablation process given that Hernandez et al. demonstrated a decrease in generation current (J_G) and open circuit voltage (V_{OC}) with an increase in laser pulse intensity [1]. Further, the non-uniform heating that can occur causes threading dislocations at the peaks of the pyramids, as deep as 1 μm [8].

The removal of SiN_x with sufficiently high laser powers for film ablation has been shown to affect the mechanical and electrical performance of solar cells. Kluska et al. demonstrated a dependence on the pulse duration of the laser on the peel force of the contacts and showed the decrease in adhesion with an increase in pulse duration. Their work relating an increase in theoretical silicide depth with a measured decrease in pseudo-fill factor (*pFF*) and the work from Büchler et al.—relating an increase in silicide depth with laser processing—indicate the damage formed from laser processing can lead to reductions of *pFF* in solar cells from deep local nickel silicide formation after annealing [4,10].

We propose a strategy for the indirect removal of SiN_x by patterning an a-Si:H etch mask with an 800 nm 140 fs laser. Due to the nature of the laser, plasma ablation of the a-Si:H mask is achievable through the generation of energetic electrons via impact ionization [11].

2. Material and methods

To investigate the effects of direct and indirect ablation of SiN_x on smooth and textured c-Si we experiment with two different processing schemes.

All substrates were p-type mono-crystalline boron doped wafers with a bulk resistivity of 1–3 Ω·cm with a thickness of 170–200 μm. Bulk resistivity of the substrates and emitter sheet resistances are determined with a Kelvin four point probe. Substrates were pseudo square and measure (156 ± 0.5) mm^2. Film depositions were performed with an Applied Materials Precision 5000 plasma enhanced

* Corresponding author at: 234 S Lakeview Blvd, Chandler, AZ 85225, USA.
E-mail address: mbailly@asu.edu (M.S. Bailly).

http://dx.doi.org/10.1016/j.tsf.2016.06.011
0040-6090/Published by Elsevier B.V.

chemical vapor deposition (PECVD) tool. All films were deposited with the conditions listed in Table 1.

The film stack of SiN_x and a-Si:H shown in Fig. 1(a) is deposited in two identical, but separate chambers of the PECVD tool (connected via a loadlock) with the conditions listed in Table 1. Sequential processing of these films in the same chamber is possible, but was not explored due to possible film flaking issues. Film thicknesses of SiN_x and a-Si:H are inferred from a weekly statistical process control of deposition rates measured by reflectance measurements of SiN_x on polished surfaces. For textured surfaces, deposition rates are divided by a factor of 1.6 that was determined by measuring the film thickness using a cross sectional scanning electron microscope (SEM) image.

Laser processing of the thin films is performed with an 800 nm 140 fs laser with a repetition rate of 5 kHz. Each repetition of the laser generates a pulse train of approximately 6 laser pulses separated by 12.5 ns. All SiN_x films are deposited with a film thickness of ~80 nm and a-Si:H films are varied from 5 to 40 nm in thickness.

Intensity control of the laser is managed using neutral density reflective filters. When fine control is required, multiple filters are used causing pulse echoing ≤1% of the transmitted power. We neglect this effect as we attribute the ablation process to the peak laser intensity—not the absorbed power—which remains unaffected by sub-peak intensity pulse echoing. Pulse overlap is controlled by the scanning speed of the flying optics used to steer and focus the laser over the Si substrate.

For clarity, we define ‘partial ablation’ as film removal over the defined laser spot area less than 70%. Regions covered in a thin layer of SiN_x are considered as non-removed sites and are observable in the SEM images presented. All SEM images are produced with a Hitachi S7800 low-voltage SEM with an acceleration voltage of 3 kV and beam current of 10 μA.

Fig. 1(a) details the processing scheme for direct removal of SiN_x. Direct removal of the SiN_x at lower power conditions with an 800 nm photon occurs via vaporization of the underlying Si due to the lack of photon absorption in the SiN_x (as shown in Fig. 2). Vaporization of the substrate can be a damage-intensive process, especially with the laser intensity variation introduced on textured substrates. Fig. 1(b) illustrates the proposed indirect removal process of SiN_x.

By using a film that can directly absorb the laser under normal conditions, it is possible to remove that film without relying on vaporization of the underlying c-Si substrate. Once the laser sensitive a-Si:H mask is patterned with the laser, the SiN_x can be patterned with a Buffered Oxide Etch (BOE) owing to the chemical etching of SiN_x in hydrofluoric acid (HF).

3. Theory

Given the high intensity and short duration of our femtosecond laser, we calculate and report the instantaneous intensity of the laser as shown in Eq. (1) using the assumption that the laser has a flat-top profile (neglecting a ~32% power variation within the full-width-half-max measured spot size).

$$P_d = \frac{P_{avg}}{(n * t_p * f)} \quad (1)$$

Table 1
Deposition conditions for thin films deposited with PECVD, SiN_x was deposited dilute in N_2 with no additional hydrogen.

Film (type)	Pressure (Pa)	Power density (W/cm^2)	Temperature (°C)	SiH_4/NH_4	SiH_4/H_2
SiN_x	460	0.75	350	1	N/A
a-Si:H	430	0.15	300	N/A	0.2

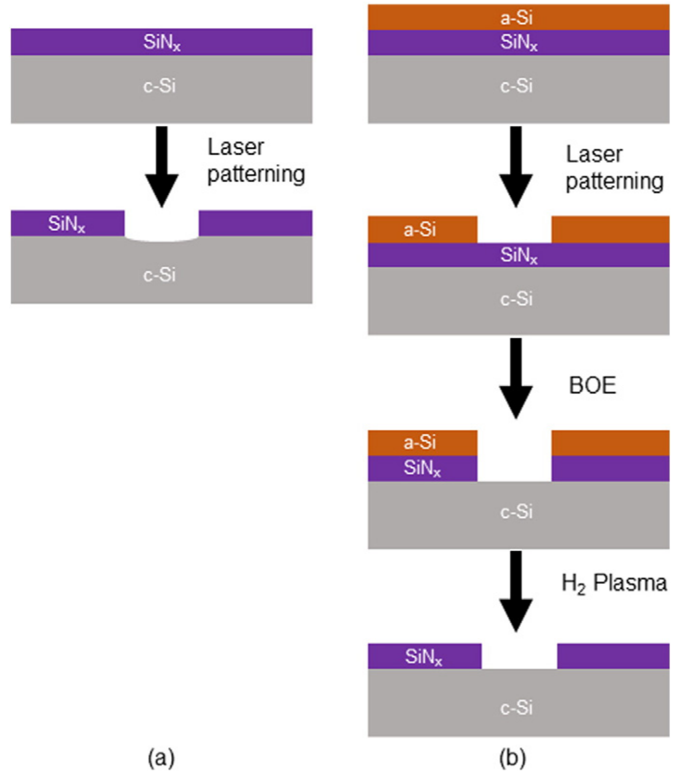

Fig. 1. Processing scheme for laser removal of SiN_x, (a) direct laser removal of SiN_x with the laser, (b) indirect removal of SiN_x using a laser ablated a-Si:H etch mask and Buffered Oxide Etch (BOE).

Here P_d is the instantaneous power density, P_{avg} the measured time average power, n the number of triggered pulses per pulse train, t_p the duration of the pulse, and f the frequency of the pulse trains from the laser system.

The intensity variation of the laser with a textured substrate complicates the power optimization process for our direct and indirect SiN_x removal processes. For the direct removal process an increase in the film removal is accompanied by a corresponding increase in damage. For our indirect removal process, we use undercutting—etching of SiN_x beneath the a-Si:H mask at the laser opened sites—to compensate for residual film. Undercutting of the

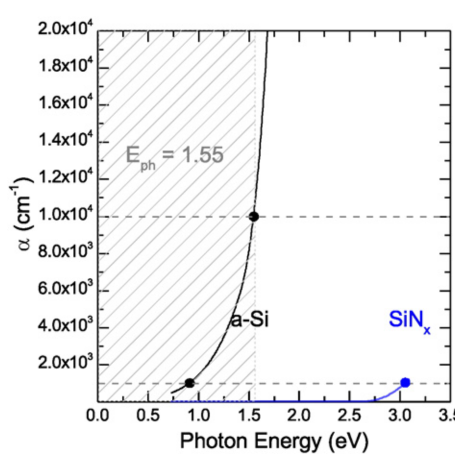

Fig. 2. Absorption coefficient plot of PECVD SiN_x and a-Si:H compared to the photon energy of the laser. The crosshatched region indicates the regime where the laser is absorbed and the horizontal dashed lines indicate the lower and upper absorption coefficient thresholds of 10^3 and 10^4 cm^{-1} for determination of an empirical optical bandgap [12].