

Title	Cat-CVD a-Si:H膜へのFLAによるpoly-Si:Hの形成と薄膜シリコン太陽電池への応用
Author(s)	Wang, Zheng
Citation	
Issue Date	2024-09
Type	Thesis or Dissertation
Text version	ETD
URL	http://hdl.handle.net/10119/19402
Rights	
Description	Supervisor: 大平 圭介, 先端科学技術研究科, 博士

氏名	WANG ZHENG		
学位の種類	博士 (マテリアルサイエンス)		
学位記番号	博材第 591 号		
学位授与年月日	令和 6 年 9 月 24 日		
論文題目	Cat-CVD a-Si:H 膜への FLA による poly-Si:H の形成と薄膜シリコン太陽電池への応用		
論文審査委員	大平 圭介	北陸先端科学技術大学院大学	教授
	徳光 永輔	同	教授
	大島 義文	同	教授
	赤堀 誠志	同	准教授
	葉 文昌	島根大学	教授

論文の内容の要旨

The use of solar energy has always been a priority in order to solve environmental issues. Of a wide variety of solar cells, crystalline silicon (c-Si) solar cells have been utilized most widely. Thin-film polycrystalline Si (poly-Si) solar cells, expected to be one of the future low-cost solar cells, require only a few μm of Si material. We use flash lamp annealing (FLA) to crystallize amorphous Si (a-Si) in a millisecond range duration using pulsed light from a xenon lamp. We have thus far demonstrated the formation of phosphorus doped n-type polycrystalline Si (n-poly-Si) films by crystallizing precursor hydrogenated P-doped a-Si (n-a-Si:H) films by FLA on Silicon nitride (SiN_x)-coated textured glass substrates. The doping concentration can be controlled and consistent before and after crystallization. We have also confirmed that explosive crystallization (EC) occurs during FLA. The potential of the absorption layer is estimated by fabricating a test cell with a simple back-contact structure. This test cell can estimate the J_{sc} and the V_{oc} . To investigate the potential of poly-Si formed by FLA, I fabricate and characterize the test cells. I used Corning Eagle XG glass substrates. Texture patterns were formed by reactive ion etching. Silicon nitride (SiN_x) and several μm -thick n-a-Si:H with a P concentration $\sim 2 \times 10^{17} \text{ cm}^{-3}$ were deposited on the textured glass substrates by Cat-CVD. After crystallizing by FLA, I performed Cat-CVD hydrogen treatment (Cat-HT) and electric furnace heat treatment for 30 min for defect reduction. I deposited Cat-CVD i-a-Si:H bilayer films and p⁺-a-Si:H emitter layer to create a p/i₁/i₂-a-Si:H stacked structure for solar cells. Minority carrier lifetime (τ_p) of crystalized Si films was characterized by μ -PCD method. ITO film was deposited by sputtering. A Kapton tape with a diameter of 8 mm was stuck on the ITO film, and then the sample was immersed in $\text{HNO}_3/\text{H}_3\text{PO}_4/\text{HF}/\text{H}_2\text{O}$ solution to etch ITO and a-Si:H layers. An Al electrode was deposited thereon by vacuum evaporation. Suns- V_{oc} measurement was also performed to extract V_{oc} and pseudo fill factor (pFF).

The i-bilayer structure significantly improved the τ_p compared to the sample with p/i₁ film. This is attributed to be due to the annealing of the i₁ film by increasing the substrate temperature (T_{sub}) in the second layer, which causes the termination of dangling bonds on the n-poly-Si surface by migrated hydrogen in the first layer. This result suggests that stacked a-Si:H passivation on n-poly-Si films is useful for improving solar cell characteristics. However, excessively thick a-Si:H increases parasitic absorption and series resistance, leading to the degradation of solar cell characteristics. Further

improvement of carrier lifetime is expected by selecting appropriate film thickness and depositing low-defect passivation films. An increase in V_{OC} by using the i-bilayer structure can also be confirmed in the Suns- V_{OC} curves. The low pFF value of 0.60 also indicates the poor surface passivation effect of the single i-layer. By using the i-bilayer, the pFF improves to 0.70, which is 0.10 higher than that obtained for the single i-layer. The V_{OC} of the cell with a single i-layer passivation film was 0.2 V, whereas the V_{OC} of the cell with i-bilayer improved to 0.44 V. This result adequately suggests that stacked a-Si:H passivation of n-poly-Si films is useful for improving solar cell properties.

In the heat treatment results. The τ_p increases gradually with increasing annealing temperature, improving significantly at 450 °C and decreasing at higher temperatures. τ_p increase is due to the increased diffusion length of H atoms at higher treatment temperatures, as well as the dissociation of H₂ molecules and the number of H atoms to bond DB in the Si film increases. On the other hand, when the annealing temperature exceeds 450 °C, the Si-H bonds are broken and the effect of H termination is lost, resulting in a significant decrease in τ_p . It is considered that low temperature and short annealing time are insufficient to terminate DB, while high temperature and long annealing time result in a large amount of H loss in the film due to Si-H bond break. Therefore, I confirmed that heat treatment is effective in reducing defects in n-poly-Si. Using the hydrogen present in the n-poly-Si film, a passivation performance equivalent to that of the i-a-Si:H stacked structure was obtained after heat treatment. A V_{OC} value of about 0.40 V was achieved with heat treatment. In Cat-HT, the effects of T_{sub} , pressure, hydrogen flow rate, and processing time of Cat-HT on τ_p of n-poly-Si thin films were investigated, and it was found that HT by Cat-CVD system is effective for defect termination. Cat-HT improved test cell characteristics. J_{sc} improved from 0.005 mA/cm² to 0.06 mA/cm² due to the termination of DB at grain boundary defects. In addition, V_{OC} due to defects in the cell grains and grain boundaries before Cat-HT improved from 0.30 V to 0.44 V.

Keywords: Cat-CVD (Catalytic Chemical Vapor Deposition), FLA (Flash Lamp Annealing), Simple back contact solar cell, Passivation, Defect reduction.

論文審査の結果の要旨

非晶質シリコン(a-Si)膜への短時間加熱による結晶化で形成される薄膜結晶シリコン(poly-Si)は、低い製造エネルギーでの作製が可能なことから、汎用の Si ウェハを用いた太陽電池に対して優位性がある。特に、キセノンランプからのミリ秒台の瞬間放電を利用した短時間加熱であるフラッシュランプアニール(FLA)は、生産性が高いことに加え、爆発的結晶化(EC)と呼ばれる高速横方向結晶化が発現するなど、興味深い特徴も有する。一方、この手法で形成した水素化 poly-Si (poly-Si:H)膜を用いた太陽電池は、膜内および膜中でのキャリア再結合が大きく、開放電圧(V_{oc})が低い問題があった。本研究は、FLA で形成する poly-Si の低欠陥化技術の開発とその太陽電池応用に取り組んだものである。

まず、poly-Si 膜と金属膜の直接接触を避けるため、窒化 Si 膜を堆積したガラス基板上への poly-Si:H 形成を試みた。反応性イオンエッチングにより凹凸を形成したガラス基板を用いることで、膜剥がれなく結晶化が可能であることを実証した。また、この結晶化が EC により起きること、前駆体非晶質 Si 膜のドーピング量により横方向結晶化速度が変化することも見出した。

次に、形成される poly-Si:H 膜でのキャリア再結合を抑制する手法として、触媒化学気相堆積(Cat-CVD)による poly-Si:H 表面へのノンドープ水素化非晶質 Si パッシベーション膜(i-a-Si:H)の堆積を実施した。堆積条件の異なる二種類の i-a-Si:H 膜を積層することにより、高い少数キャリア寿命が実現できることを見出した。さらに、膜中に残留する水素原子や、外部から供給する原子状水素を利用した Si 膜中の未結合手の終端についても検討した。この結果、適切な条件でのポストアニールや、Cat-CVD 装置で生成される原子状水素への poly-Si:H 試料の曝露により、少数キャリア寿命が大きく改善することを確認した。

これらの手法を適用した poly-Si:H 膜を用い、薄膜 poly-Si 太陽電池を形成し、その特性を評価した。キャリア再結合に敏感なパラメータである V_{oc} に着目して評価を行ったところ、上述の積層 i-a-Si:H によるパッシベーションや Cat-CVD による原子状水素処理を組み合わせることにより、FLA で形成した poly-Si:H 膜を用いた太陽電池で、Si ウェハを用いた市販の結晶 Si 太陽電池に匹敵する、0.6 V 程度の V_{oc} が得られることを実証した。

以上、本博士論文では、FLA により形成した poly-Si:H の低欠陥化法について確立し、太陽電池性能の向上に成功しており、学術的に貢献するところが大きい。よって博士(マテリアルサイエンス)の学位論文として十分価値あるものと認めた。