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論文の内容の要旨

Passivating contact, which is proposed to reduce surface recombination at metal-semiconductor interface, has been improved throughout Si solar cell development. The metal-semiconductor direct contact has been minimized as much as possible in PERC (passivated emitter and rear contact) solar cells. However, TOPCon (tunnel oxide passivated contact) has been received a lot of attention for its simple processing and high efficiency which achieved by its full passivated contact using an ultra-thin oxide and heavy-doped silicon layer. Cat-CVD (Catalytic Chemical Vapor Deposition) is suitable for making passivation films for its nature of no plasma-induced damage. Compared with the oxide films forming methods of TOPCon, single-sided film formation is a merit of Cat-CVD silicon nitride (SiNx). Considering the difficulty of Cat-CVD oxide film deposition, we use Cat-CVD SiNx films as the tunneling layer for a new type called TNPCon (tunnel nitride passivated contact).

The first step is to correctly evaluate the thickness of SiNx films. TEM images show that the actual thickness is thinner than the results of ellipsometry. However, the deposition rate can still be confirmed by massive data from ellipsometry. After evaluating the thickness of ultra-thin SiNx films, symmetrical TNPCon samples were made to study its passivation quality and conductivity. The relationship between contact resistance (ρC) and SiNx thickness indicates that the tunneling effect dominates the conduction of TNPCon below 2.5 nm and is drastically weakened by thicker SiNx films. In addition, the SiNx thickness also affects the passivation quality of TNPCon. TNPCon samples with 1.6 nm SiNx films achieved an effective minority carrier lifetime (τeff) of more than 800 ms. TNPCon samples with thicker SiNx films show lower τeff, one possible reason is due to phase separation in SiNx films during high temperature annealing. In addition, SiNx films prevent the diffusion of phosphorous (P), which shows in the higher sheet resistance of TNPCon samples with thicker SiNx films. With introduction of H2 during deposition, the crystallinity of the heavily doped silicon (n+-Si) films increases, which is considered to be n+-μc-Si containing a small amount of hydrogen. From the SIMS depth profiles, the P doping concentration was determined, and the optimal doping concentration for TNPCon is about 2%, because over doping would lead to the degradation of n+-Si films. It is also necessary to ensure that the thickness of n+-Si is greater than 12 nm which is related to the carrier selectivity of n+-Si films. In addition, the optimal annealing condition was also confirmed, which is annealing at 850 °C for 1 hour.

In order to further improve the passivation quality of the TNPCon, catalytically generated atomic hydrogen (Cat-H) was used for its hydrogenation process. Cat-H has a strong etching ability on silicon, regardless of crystal from of silicon. If there were no surface thermal silicon oxide films formed during high temperature annealing, n+-Si layer of TNPCon/TOPCon will be etched away. But this unexpected thermal oxide films protects n+-Si layer and does not block the diffusion of hydrogen atoms. From the SIMS depth profiles of TOPCon samples, the H diffusion curve is interrupted at the Si/SiO2 interface where a large amount of hydrogen atoms accumulate. H accumulation indicates termination of defects in Si/SiO2 interface which is thought to be responsible for the improvement of passivation quality.

However, the improvement of TOPCon is far more obvious than that of TNPCon. After comparing their P diffusion depth profiles, the increased Auger recombination caused by thicker n+-Si layers was considered the most likely reason.

In Cat-CVD apparatus, ammonia decomposed species (Cat-N) lead to direct surface nitridation of Si, which is also used to prepare ultra-thin SiNx films in TNPCon. Insufficient thickness of Cat-N SiNx films and heavily doped Si layer caused unprecedented low sheet resistance of TNPCon samples. Considering that the Auger recombination in n+-Si layers will damage the quality of passivation, the SiNx film with the ability to prevent P diffusion during high temperature annealing becomes the purpose of further research. One direction is to increase the substrate temperature during Cat-N nitridation, which can also improve the current problem of insufficient film thickness. Another direction is to change the deposition conditions of SiNx films.

Keywords: Passivating contact, Cat-CVD (Catalytic Chemical Vapor Deposition), Ultra-thin silicon nitride, TNPCon (tunnel nitride passivated contact), Cat-H (catalytically generated atomic hydrogen) hydrogenation, Direct nitridation.

論文審査の結果の要旨

結晶 Si 太陽電池の高性能化のために、Si 表面での少数キャリアの再結合を抑制しつつ、多数キャリアの流れも阻害しないパッシベーションコンタクトとよばれる構造がさかんに研究されている。最も普及しているものの一つに、極薄トンネル酸化 Si 膜を用いた tunnel oxide passivated contact (TOPCon)構造があるが、現行の製膜法では酸化 Si 膜が Si 基板両面に形成されてしまうため、事後の除去工程が必要であった。使用する極薄トンネル膜を、触媒化学気相堆積(Cat-CVD)で堆積する窒化 Si (SiN_x)に代替することで、片面のみへの製膜が可能となるうえ、Cat-CVD の特長である基板へのダメージの少ない製膜がもたらすパッシベーション性能の向上、酸化 Si よりバンドギャップの小さい SiN_x の利用によるトンネル伝導性の向上も期待される。本研究では、極薄 SiN_x 膜を用いた tunnel nitride passivated contact (TNPCon)の開発に取り組んだ。

Cat-CVD での SiN_x 膜堆積により、nm 台の膜厚を有する SiN_x が形成可能であることを確認した。また、この膜を用いて TNPCon 構造を作製し、実効少数キャリア寿命(τ_{eff})からパッシベーション性能を評価したところ、>800 μs という高い τ_{eff} を得た。この値は、TOPCon 構造の τ_{eff} (~2 ms)には及ばないものの、TNPCon 構造が優れたパッシベーション性能を有することを実証した。また、コンタクト抵抗からトンネル伝導性を評価したところ、<5 mΩcm^2 という太陽電池性能を低下させない程度の低い抵抗を確認し、パッシベーションとキャリア伝導の両立を実現した。さらに、SiN_x の膜厚が 2.5 nm 以下であれば、十分なトンネル導電性が得られることも明らかにした。

また、Cat-CVD での膜堆積のみならず、NH_3 の触媒分解種に Si 基板し窒化させる方法(Cat-N)により形成される極薄 SiN_x を用いた TNPCon 作製法も確立した。Cat-N は膜堆積と比べて膜厚の制御性が高く、産業応用上有利である。また、H_2 を触媒分解することにより得られる原子状水素を用いた欠陥低減処理(Cat-H)による、TNPCon および TOPCon のパッシベーション性能向上も確認した。TNPCon のパッシベーション性能のさらなる向上のために、SiN_x 上に堆積する高ドープ n 型 Si 層から結晶 Si 基板への過度のリン(P)拡散を抑制することが必要であり、そのためには、SiN_x の N 組成を増加させ、P に対する拡散バリア性能を高めることが重要であることも見出した。

以上、本論文は、結晶 Si 太陽電池の新規パッシベーションコンタクトの開発に関するものであり、学術的および工業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。