Deposition of Contaminants on Silicon Media During Wet Processing

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Abstract

The evaluation of photovoltaic manufacturing wet process steps shows how impurities may be deposited on silicon media. Upon withdrawing a wafer, a liquid layer remains on the silicon surface. Any contaminants in the liquid will be deposited on the silicon when the liquid evaporates. This data shows the biggest factor affecting deposition of impurities is the concentration of impurities in the bath.

The introduction of contaminants on silicon media during processing can reduce the efficiency of photovoltaic (PV) cells and shorten their lifetime. One of the sources of contamination is process baths, where media is dipped into water and/or chemicals for etching or cleaning. The sources of bath contaminants are numerous. They can arise from insufficiently pure chemicals or water. The tanks, silicon carriers and handling equipment may be constructed from industrial-grade materials that desorb impurities, thereby contaminating baths. Alternatively, the impurities could be extracted from common plastics used in industrial-grade plumbing components or chemical containers.

The following information discusses an examination of how a contaminated process bath may potentially deposit impurities on silicon media. Upon withdrawing a silicon wafer from a bath, a thin layer of liquid is left on the surface of the silicon, as depicted in Figure 1. Any contaminants in the liquid layer will be deposited on the silicon when the liquid evaporates. This information will show that the biggest factor affecting deposition of impurities is the concentration of impurities in the bath. Other factors such as removal speed of the wafers from the bath and properties of the liquid including surface tension, density and viscosity are less influential.

Sources of Contamination in Wet Processing

Processing of silicon wafers into photovoltaic cells involves multiple steps. The process starts out with growing the silicon ingot and proceeds through various steps including wafer sawing, cleaning, etching, diffusion, screen printing and finally testing. Throughout this process, it is crucial to maintain the purity of the silicon wafer, as it has been shown that contamination can negatively impact the cell's efficiency and effective life.

Pre-diffusion wet processes are one source of contamination in the manufacturing process. These wet processes typically use high-purity chemicals such as hydrofluoric acid (HF) and hydrochloric acid (HCl), along with 18 megohm cm deionized (DI) water. While the chemicals start out with low impurities, the chemical's exposure to materials used in the chemical distribution system such as pipes, valves and containers can contaminate the liquids to unacceptable levels. Extractable testing has shown that the type of material used for wetted components such as polyvinyl chloride (PVC), polypropylene (PP) or perfluoroalkoxy (PFA) has a significant impact on the level of contamination present in the fluid media.[1]

The concern over contamination is compounded in wet benches where chemical baths are often recirculated

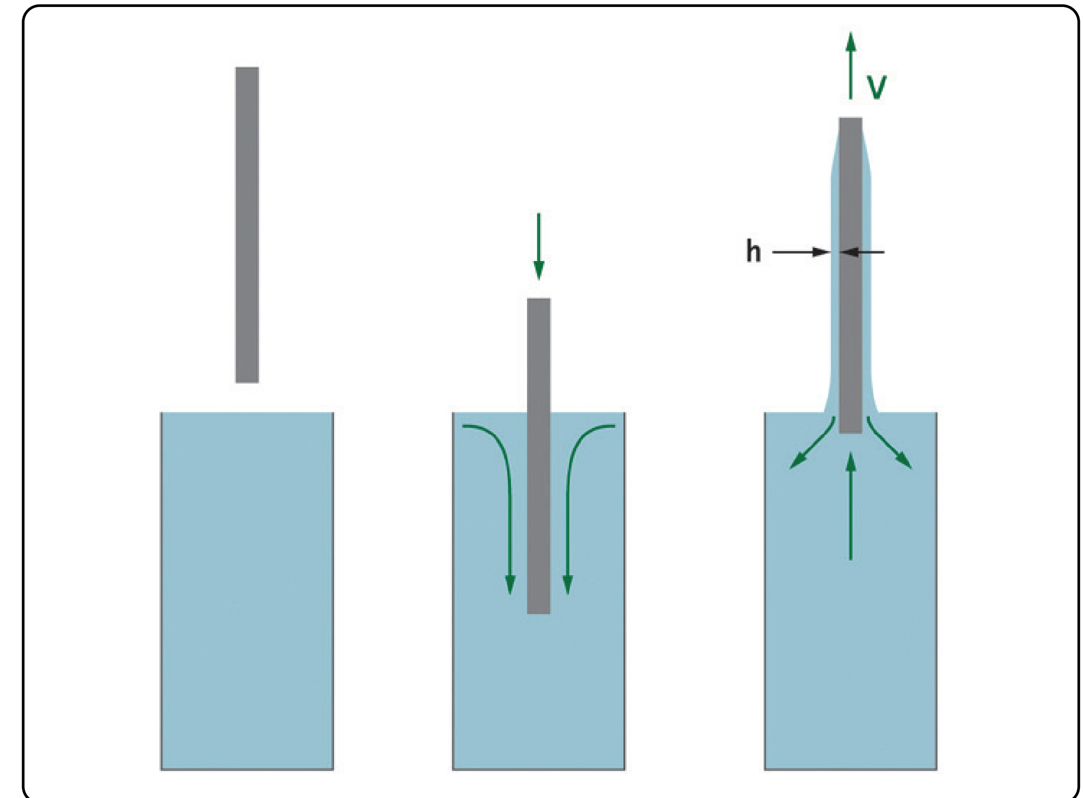

Figure 1 – Wafer Submersion and Withdrawal From a Process Bath *Data source: Entegris*

without the use of filtration, causing the contamination levels to grow over time.

Once a process bath becomes contaminated, it leads to the transfer of these impurities onto the surface of the silicon wafer. This is accomplished through the submersion and withdrawal of a silicon wafer from a process bath. During submersion of the wafer into a specific liquid media, the chemical and its constituents surround the wafer. Upon removal of the wafer from the liquid media, a layer of the chemical will remain on the surface of the wafer. This layer of liquid will contain the desired chemical elements but will also contain contaminants found in the liquid. As the liquid evaporates, the impurities found within the liquid will remain on the surface, resulting in increased levels of contamination on the silicon wafer.

It is well known that metallic contaminants have a significant effect on carrier lifetimes. Metallic contaminants can be introduced into the bath as byproducts of etching/texturing of the silicon and can also be introduced through process. Many studies have been conducted to measure the effects of metal contaminants on cell performance.[2-4] The majority of these focused on iron bulk contamination in the silicon substrates.[2,3] Metal contaminants with planar (or surface) concentrations on the order of 10^{11} atoms/cm^2 have been shown to change carrier lifetimes by more than an order of magnitude.[4] Most, but not all, of this loss can be recovered through appropriate thermal processing. As a result, minimization of metal contamination is critical in achieving maximum carrier lifetimes and cell efficiencies.

Calculating Contamination On Silicon Wafers

Utilizing techniques and theories common to the dip-coating process, the chemical thickness layer remaining on a silicon wafer after removal from a liquid bath can be calculated. The thickness of the liquid layer (*h*) can be estimated from the Landau-Levich equation,

$$h = 0.946\left(\frac{\gamma}{\rho g}\right)^{1/2}\left(\frac{\eta V}{\gamma}\right)^{2/3}$$

where *V* is the withdrawal velocity of the silicon substrate, *g* is the acceleration due to gravity and γ, ρ and η are the surface tension, density and viscosity of the liquid.[5,6] The Landau-Levich equation has been shown to accurately predict the thickness of liquid layers for solid surfaces that are withdrawn at velocities such that $\eta V/\gamma < 0.01$-0.1 and have zero or near-zero receding contact angles.

Using the residual thickness along with the liquid contamination level, it is possible to quantify the contamination level increase on a wafer as a result of the impurities in the liquid bath. The surface concentration of contaminant on the wafer (Γ) is proportional to the liquid film thickness (*h*) and the bulk concentration in the liquid (*c*).[7]

$$\Gamma = hc$$

Using this approach, the data generated shows the contamination level increase on a silicon wafer after exposure and removal from a wet process bath. Figure 2 shows the thickness of the film (*h*) left on a wafer after removal from a 25°C water bath as a function of the withdrawal velocity (*V*). As *V* increases, so does the film thickness. Film thickness is quite sensitive at lower speeds, but becomes less dependent at higher velocities. As the chemicals used in wet processing have similar surface tensions and densities, changing the liquid or its properties via additives would have a modest effect on the thickness of the liquid film.

Because the viscosity of liquids is quite sensitive to change in temperature, increasing the temperature of the bath can have a dramatic influence on the film thickness. Figure 3 shows the thickness of a water film that remains after dipping a wafer in a water bath at various temperatures (*T*). As the temperature rises, film thickness decreases with falling viscosity. For example, at *V* = 100 mm/s, *h* decreases from more than 30 µm to less than 20 µm as *T* increases from 25° to 60°C.

Figure 4 shows the predicted concentration of surface contaminant (Γ) as a function of the concentration of the contamination in the bulk liquid (*c*) at room temperature (25°C). For a given withdrawal velocity, the surface contamination increases proportionally with the amount of contaminant found in the bulk liquid.

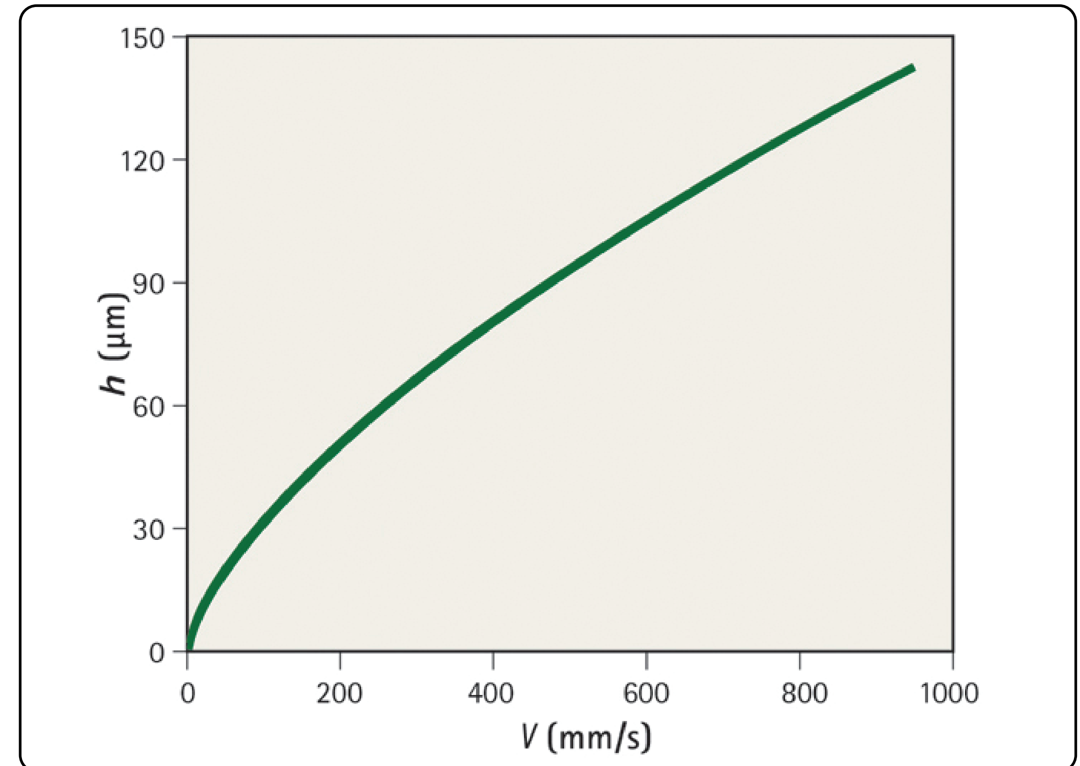

Figure 2 – Thickness of the Film (*h*) Left on a Wafer After Removal From a 25°C Water Bath as a Function of the Withdrawal Velocity (*V*). *Data source: Entegris*

Note the relatively weak dependence on withdrawal velocity. For a bath with a bulk contaminant concentration of c ~ 1000 ng/L (or ~ 1 ppb) and a withdrawal rate of $V = 100$ mm/s, the amount of contaminant left behind on the wafer is approximately 5×10^{-3} ng/cm^2. If the contaminant were iron, then the expected surface coverage would be ~ 5×10^{-11} atoms/cm^2, which has been shown to change carrier lifetimes by more than an order of magnitude.[4]

These results will allow a photovoltaic manufacturer to fully understand the impact the purity level of their wet process baths have on the contamination level present on their wafer. It will also help PV manufacturers to improve the purity of their wafers through better control of their wet process steps.

Conclusion

It has been shown that impurities found in a photovoltaic cell can reduce the cell's efficiency. Iron contamination, for example, will reduce the minority-carrier lifetime resulting in lower cell efficiency. Consequently, it is functionally and financially important to protect the silicon wafer from contamination during the manufacturing process. The data shown in this paper demonstrates the increase in contamination on a silicon wafer due to the impurities found in the wet processes. This will allow photovoltaic manufacturers to evaluate their own wet process baths and understand the impact they have on their wafer purity levels.

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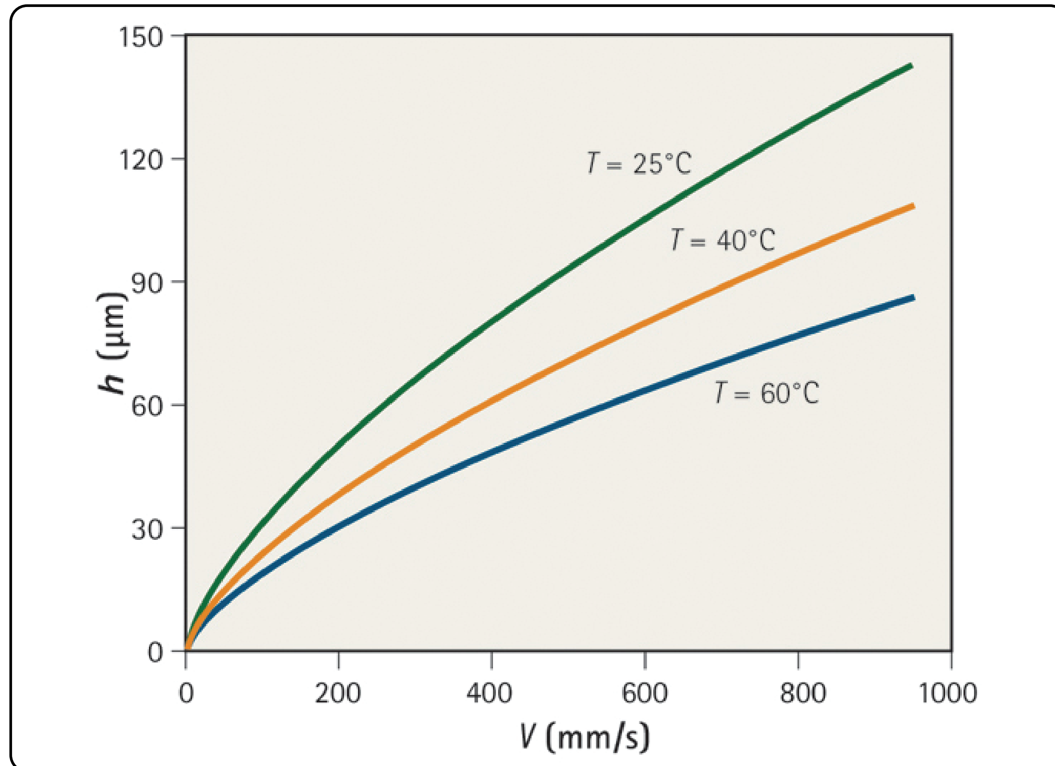

Figure 3 – Thickness of the Film (*h*) Left on a Wafer After Removal From a Water Bath at Various Temperatures (*T*). *Data source: Entegris*

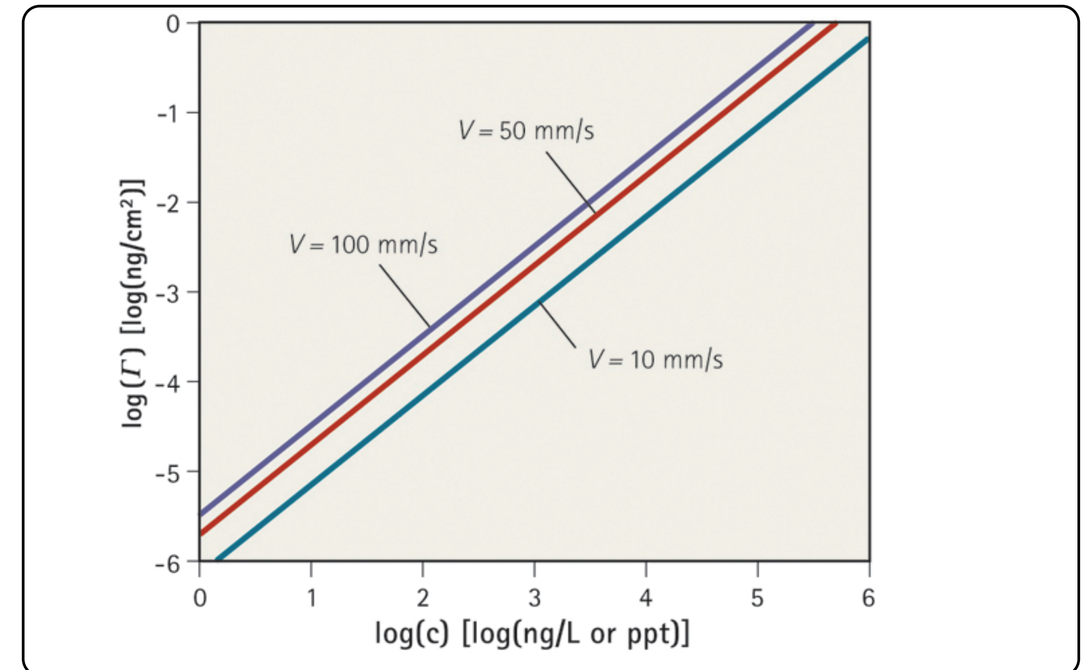

Figure 4 – Concentration of Surface Contaminant (Γ) as a Function of the Concentration of the Contamination in the Bulk Liquid (c) for Three Different Withdrawal Velocities (V). *Data source: Entegris*

This article first appeared in Future Photovoltaics, Issue 5 © 2011, www.FuturePV.com, published by Mazik Media, San Francisco, CA.

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