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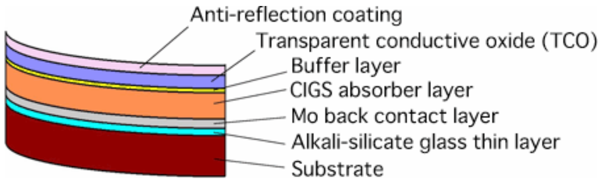
DUV Picosecond Fiber lasers for Thin-film Photovoltaic's

Introduction

Thin-film photovoltaic (PV) coatings on inexpensive substrates are expected to be a significant contributor to the reduction in cost of solar energy. To achieve this goal, significant improvement in the cost, conversion efficiency and yield of thin-film cells must be realized.

Thin-film Photovoltaics

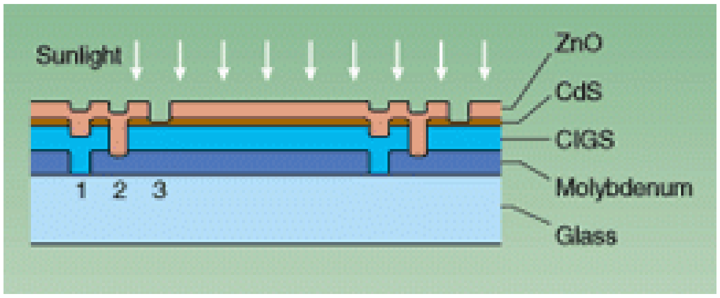
There are four primary thin-film PV technologies, hydrogenated amorphous silicon (a-Si:H), copper indium diselenide (CIS), copper indium gallium diselenide (CIGS)and cadmium telluride (CdTe). In each of these technologies, laser patterning is a critical step in producing monolithic integration of cells into large-area panels.



Sunlight falls on the earth's surface with an intensity of about 1 kW/m², so that a 1m² solar cell operating at 10% efficiency is capable of producing 100 W of electrical energy. The electrical current from each PV cell scales with its area, but its output voltage is typically 60% of the bandgap energy of the semiconductor material employed. Typical output voltages are 0.6V for Si and CIS/CIGS, 0.8V for CdTe, and 1.0V for a-Si:H. This voltage is independent of the cell area. As an example, a 10% efficient CdTe cell of 1m² producing 100 W of power would develop 125 A of current. Current this high would require the current-carrying bus lines to be prohibitively thick and the transparent conducting oxide used for one of the electrodes in each of the thin-film technologies is too resistive.

The conventional solution is to form the thin-film structure into smaller cells and provide series interconnections. This way, the same 1m² film with 100 integrated cells produces only 1.25A at 80V but yields the same power as the larger cell. The challenge is to achieve the interconnections with the smallest possible loss of thin-film real estate with optimum yield. Rather than using individual wire bonded connections, as is done for c-Si PV wafers, this is done monolithically during the fabrication of the thin-film panel.

Thin-film PV Manufacturing



The standard interconnection for thin-film PV cells is a three-step patterning series. Patterning, or scribing, is the process of producing a well defined trench in one or more layers of film or substrate. The first scribe, called P1, divides the conductive coating on the glass, typically 500nm thick, into electrically isolated regions. The second P2 scribe, done after deposition of the 2-3μm semiconductor layer, provides the interconnect path, or via, through which the final conductive coating contacts the bottom electrode. The third P3 scribe cuts the 500nm top electrode to isolate the cells and complete the fabrication into a series-interconnected structure. This three-scribe pattern is repeated approximately every centimeter.

A successful interconnection must have both low series resistance and high shunt resistance. Residual semiconductor material or an oxide layer left at the bottom of the via will lead to unacceptable series resistance. Shunting will occur if occasional bridging material is left after either of the isolation scribes (number one or three), because these two layers are highly conductive. Shunting and excessive series resistance are two of the primary killer defects limiting thin-film conversion efficiencies and yields.

Thin-film Scribing Requirements

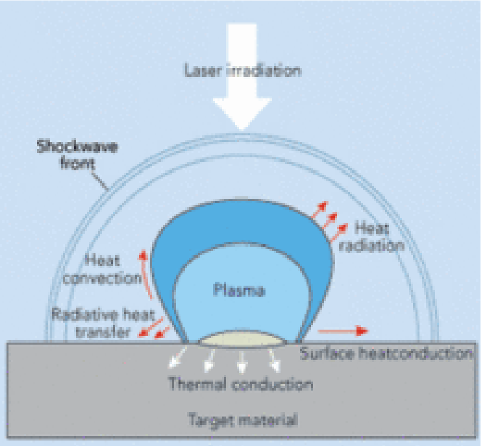
To attain economic viability, thin-film devices must be produced in high volume for low unit cost. High throughput is critical to minimizing scribing costs. Precision scribes with very low defect count are also necessary to deliver a high yield of final product with the highest possible electrical conversion efficiency.

To achieve the scribing objectives, both resolution and precision are required. Specifically, the area between P1 and P3 is a non-active area. Scribe lines are currently on the order of 10-30microns in width, with an offset separation between P1 and P3 of hundreds of microns. Given that each cell has a total width of 10 mm, and the necessity of maximizing the conversion efficiency, it is vital to minimize the scribe area. This means minimum width scribes that are placed as close to each other as possible, with minimum offset, are essential.

Scribe quality in terms of cell efficiency yield is another important consideration, because cell conversion efficiency is substantially reduced by scribe induced defects. Edge roughness, layer peeling, micro cracks, shunting, excessive series resistance and other types of surface and subsurface thermal damage can result in significant cell efficiency degradation. Therefore, it is vital to create scribes with precise depth control, minimum scribe width, complete material ejection, minimal heat generation and smooth edges at high throughput speed.

Laser ablation has emerged as the best-of-breed technology of all scribing processes, as it is critically enabling high-volume production of next-generation thin-film devices, surpassing mechanical scribing methods in quality, speed, and reliability.

Laser Ablation Physics

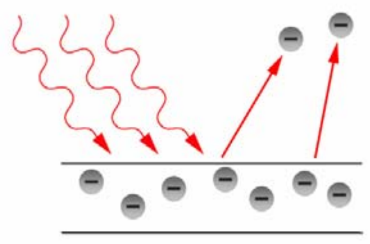


Laser ablation is the process of removing material from the thin-film surface by irradiating it with a laser beam. When the laser pulse is absorbed by the target, energy is first converted to electronic excitation and then to thermal and mechanical energy resulting in plasma formation and ejection. The ejected species expand into the surrounding area in the form of a plume which may contain electrons, ions, neutral atoms, molecules, and clusters.

Ablation begins with incident photons (light particles) giving up their energy to the electrons in the target material. All of the pulse energy is absorbed in a volume dictated by the spot size and the penetration depth. Longer wavelength light generally has a greater penetration depth (> 10 micron) than DUV light, which is absorbed in a relatively thin layer (< 20 nm). This effect helps to concentrate UV light energy and provide depth control.

Upon absorption of incident light, some electrons move to higher energy levels (photo-ionization) but remain below the energy threshold necessary to escape the material. Other electrons may receive enough energy that they may actually escape the material (photo-emission). Energetic electrons within the material may absorb even more energy from additional photons, and may excite more ground state electrons by electron-electron collisions, resulting in an "avalanche" of energetic electrons. In semiconductors and insulators, in order to receive energy at all, an electron must interact with enough photons to boost the electron over the material band gap. A significantly higher minimum energy threshold is required to remove the electron from the material through photoemission. One can see that the shorter the wavelength of the laser light, the fewer photons must interact with an electron at (nearly) the same time for photo-ionization or photo-emission to occur.

To ablate the material, ions or atoms must be ejected from the surface. There are several known mechanisms by which this occurs. We can loosely categorize these processes as thermal or non-thermal. In thermal processes, energy from the excited electrons is transferred to the atomic lattice via electron-phonon interactions. The atoms heat up, and material may be ejected by a variety of equilibrium or non-equilibrium processes such as boiling or spalation. In non-thermal processes, atoms are ejected before sufficient time has elapsed to allow electrons to significantly transfer energy to the lattice vibrational states (acoustic phonons). The time scale for this process is around 5-50 ps. Both thermal and non-thermal processes may occur sequentially or even simultaneously for a single pulse. Thermal processes are not necessarily restricted to nanosecond pulse durations, they may also be the dominant mechanism for longer wavelength picosecond and femtosecond pulses. In the latter case, the ablation takes place after the incident light flux has ceased.



There are at least two distinct major types of non-thermal ablation pathways: ultrafast phase change and Coulomb explosion. Ultrafast melting is an ultrafast phase change that occurs in semiconductors when the proportion of electrons that are photo-ionized into the conduction band is above a critical threshold. Since the ground state valence band electrons are involved in bonding orbitals which hold the atomic lattice together, photo-ionization and photo-emission can be thought of as a bond breaking processes. When enough bonds are broken, the ordered lattice collapses into an energetic liquid. If the intensity of light is much higher (~ 10^13 W/cm^2), enough bonds may be broken that material undergoes a direct solid-plasma transition. Achievable for femtosecond pulses, this ultrafast phase change process results in a dense, hot (10^6 K) plasma that then expands.

Coulomb explosion is an ablation process that occurs when the rate of photo-emission is high enough to leave a large net positive charge at the surface of the material. Electrostatic repulsion of the surface ions blasts them out of the material. Experiments in which Si was exposed to nanosecond pulses of deep UV (193 nm) light has shown that Coulomb explosion occurrs before any other type of ablation as the fluence was increased. Coulomb explosion is suppressed when the electrical conductivity of the excited material is large enough that the influx of electrons from the bulk keeps the surface charge density below a threshold value.

All ablation processes have a threshold pulse energy which depends on material, wavelength, and pulse duration. For typical thermal processes, ablation thresholds and rates vary little as the pulse duration is reduced from several picoseconds to tens of femtoseconds. Once the peak intensity is great enough to induce ultra-fast melting, however, ablation rates increase again.

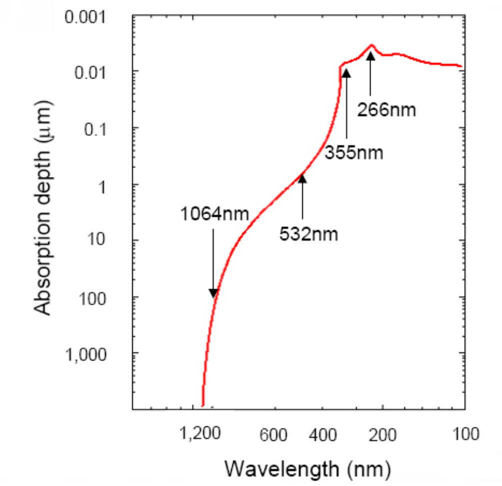
Ablation produces an ejected plasma which itself can absorb light. In this way, the ejected plasma can cause an unwanted shielding effect, in which much of the light does not reach the surface. For thermal processes, in which there is a delay of at least 10 ps between photo-ionization and lattice heating, intrapulse ablation shielding may be avoided by making the pulse duration less than the delay time. The efficacy of this mechanism depends on rep rate and the rate at which the plasma expands.

Photoionization and photoemission is differentiated from photothermal and direct thermal ablation by no heat damage below the penetration depth (~10nm); very accurate depth control; high ablation rates; large numbers of various ablated species with high translational energies (Coulomb explosion); nonequilibrium between the translational, vibrational, and rotational temperatures of ablated products; presence of shock wave propagation with high initial velocity; high gas-like plume density; fast surface swelling; and a low ablation threshold value.

Laser Wavelength Requirements

There are two thin-film manufacturing performance constraints which dictate the optimum laser wavelength for a given scribing application. The first criterion is ablation depth control and the second is photoemission.

Ablation Depth Control – As previously noted, the penetration depth of the thin-film material is highly dependent on laser wavelength. Due to the necessity to eliminate subsurface thermal damage, it is imperative to limit the photon absorption depth to a fraction of the film thickness of the target material. In the case of the conducting layers, the thickness is typically less than 500nm. In the case of the absorbing semiconductor, the thickness ranges from 1-3μm. As a result, maximum depth precision can only be achieved using a laser wavelength with very low absorption depth, taking advantage of a high pulse repetition rate to remove very thin layers with each pulse. For example, material can be removed in 50nm increments at 10MHz pulse rates with Deep Photonics FLP-0266-PPP family of lasers.



Photoemission - In order to generate dominant photoemission in a given target material, the photon energy of the laser must be greater than the work function of the material. The work function is the amount of energy necessary to eject a bound valence electron from the atomic lattice structure of the material. The work function for a given material is typically expressed in electron volts (eV) and can be conveniently converted to a corresponding photoemission wavelength. In the case of thin-film technologies, all of the current target materials require a laser wavelength less than 300nm.

For example, ZnO is a semiconductor with a direct bandgap energy of 3.37eV at room temperature. The work function energy necessary to liberate a valance electron and eject an ion from the lattice into cold plasma is 4.2eV. This corresponds to a laser wavelength of 295nm. Comparatively, for laser wavelengths longer than 295nm, zinc oxide decomposes into zinc vapor and oxygen at around 1975 °C.

PV Material		Work Function (eV)	Photoionization Wavelength (nm)
Cadmium telluride	CdTe	5.7	218
Cadmium selenide	CdSe	5.3	234
Silver	Au	4.7	264
Copper	Cu	4.7	264
Crystalline Silicon	c-Si	4.6	270
Amorphous Silicon	a-Si	4.5	276
Indium Tin Oxide	ITO	4.5	276
Molybdenum	Mo	4.3	288
Tin Oxide	SnO_2	4.3	288
Copper indium gallium diselenide	CIGS	4.3	288
Zinc Oxide	ZnO	4.2	295
Copper indium diselenide	CIS	4.2	295

As a result, the optimum laser wavelength for thin-film non-thermal ablation depth control on P1, P2 and P3 scribes is in the DUV region.

Pulse Duration Requirements

As previously noted, it is imperative to minimize the thermal damage associated with evaporation of the target material in favor of photoemission.

Plasma shielding - Once formed, plasma absorbs laser radiation by inelastic free electron scattering also called inverse-Bremsstrahlung, which results in further heating of the plasma. The absorption of the radiation by the plasma is a function of the plasma density, the plasma temperature and the laser frequency. For sufficiently long laser pulses, the electron density above the target surface can become so dense that the plasma becomes opaque and no laser-target interaction is possible. However, as the plasma expands, it becomes less dense and the laser may again interact with the target surface and in this way a self-regulating process is established. The hot plasma also emits light, partly by Bremsstrahlung at the early stage of plume expansion, but also by emission from atoms, ions and molecules, which is seen as a luminous region just above the target surface.

As a result of the high degree of absorption of DUV laser pulses due to plasma shielding, it is only possible to sustain photoemission until the plasma begins to develop. This is dictated by the energy relaxation time and is typically a few picoseconds in non-metals (metals typically have energy relaxation time of a 10 femtoseconds). Laser pulses longer than 10psec are mostly absorbed by the developing plasma resulting in direct, high temperature thermal ablation, regardless of laser wavelength. It is interesting to point out that there is minimal benefit to pursuing short wavelength DUV lasers to achieve photoemission if the technology cannot deliver picosecond pulses. In addition, there is no benefit to utilizing ultra-fast femtosecond pulses relative to picosecond pulses at an identical wavelength and pulse energy.

The practical result of the convolution of plasma physics, thin film manufacturing requirements and pulsed laser technology has lead Deep Photonics to concentrate it’s efforts developing fiber-based, picosecond DUV lasers to address these challenging requirements.

Laser Technologies

All pulsed solid-state lasers used to achieve DUV wavelengths for thin film scribing use a technique known as frequency conversion. Frequency conversion is accomplished by passing laser light at a fundamental wavelength, through a non-linear optically active crystal (NLO). Specific crystalline attributes of the NLO material cause the fundamental wavelength to be converted to half of its original wavelength; this process is known as second harmonic generation (SHG). This general technique can be used to produce additional harmonics including the third harmonic (THG) and the fourth harmonic (FHG). Most solid-state lasers used today in thin-film scribing utilize a fundamental wavelength of 1064nm, resulting in a SHG wavelength of 532nm, a THG wavelength of 355nm and a FHG wavelength of 266nm.

Pulsed laser designs come in two operating regimes, nanosecond and picosecond. Pulsed laser designs emit a time varying amplitude laser output. The rate of the amplitude variance is defined as the pulse frequency. Solid-state DUV picosecond lasers are characterized by the use of temporally short (~10ps), high intensity (>1kW), high frequency (>1MHz) pulses which pass through multiple stages of frequency conversion in a single pass. The desire for high intensity pulses is due to the non-linear nature of the frequency conversion process. The efficiency of the process is proportional to the square of the intensity of the incoming laser light. The practical limit for the number of frequency conversion stages is dictated by the maximum conversion capability, in the DUV, of the NLO crystal employed. Achieving high power FHG at 266nm with a picosecond laser strictly becomes a question of the capability of the NLO.

In contrast to nanosecond laser limitations, Deep Photonic’s DUV picosecond lasers have virtually no sensitivity to typical environmental conditions. In addition, absorption is a secondary concern; in fact most high intensity picosecond systems abandon the use of anti-reflection coatings on the DUV NLO crystals to improve component lifetime. The most striking comparison with nanosecond systems is the advantage of using picosecond pulses. Virtually all NLO’s, possess a remarkable attribute in where the damage threshold of the material increases as the inverse square root of the pulse duration. For example, if a specific material has a damage threshold of of 1GW/cm^2 at a pulse duration of 10ns, then the damage threshold at 10ps is 31 times higher, or 31GW/cm^2. This attribute, coupled with the square intensity law efficiency nature of the frequency conversion process, provides an overwhelming incentive to adopt short pulse, high intensity, high frequency laser designs as the preferred technical direction to achieve high power DUV scribing laser sources.

In order to achieve high fundamental output power, both nanosecond and picosecond lasers rely on amplification stages to exponentially increase a small signal pulse. In the case of bulk amplifier technology such as thin disk and YAG, the power amplifying stage requires multiple passes to achieve adequate gain. These amplifiers, known as regenerative, are expensive and limit the pulse frequency to a few hundred kilohertz. In contrast, Deep Photonics utilizes fiber laser technology which accomplishes amplification in a single pass of the fiber power amplifier. The fiber technology enables pulse frequencies 100 times greater than bulk amplifier technology.

Conclusion

The photovoltaic industry requires continuing improvement in thin-film scribing performance and throughput. To achieve these goals, thin film scribing systems will likely employ frequency converted, solid-state fiber lasers with DUV wavelength, picosecond pulses and higher power than they currently utilize. High peak power, picosecond pulses from a fiber laser can be frequency converted through multiple stages of wavelength conversion based on new NLO material. The resulting DUV picosecond pulses provide unparalled performance for thin-film scribing resulting in maximum cell conversion efficiency and throughput optimization.

References

M.A. Lieberman and A.J. Lichtenberg, “Principles of Plasma Discharges and Materials Processing”, Wiley 1994.
R.H. Bube, “Photovoltaic Materials”, Imperial College Press, 1999.
PV News – 2003 – 2007

D. Basting, G. Marowsky, Eds. Excimer Laser Technology, Springer Verlag, Berlin 2005.
D. Bäuerle, Laser Processing and Chemistry, 3rd Edition, Springer Verlag, Berlin 2000.
J. Ihlemann, D. Schäfer, Applied Surface Science 197-198, 856 (2002).
C. Kappel, A. Selle, T. Fricke-Begemann, M. A. Bader, G. Marowsky, Appl. Phys. B 79, 531 (2004).
A. D. Compaan, I. Matulionis, and S. Nakade, "Optimization of Laser Scribing for Thin-Film PV Modules," Final Technical Progress Report, NREL/SR-520-24842 (available from NTIS).