Electrically conductive adhesives: An emerging interconnection technology for high-efficiency solar modules

Torsten Geipel & **Ulrich Eitner**, Fraunhofer Institute for Solar Energy Systems ISE, Freiburg, Germany

ABSTRACT

Electrically conductive adhesives (ECAs) are an alternative interconnection technology especially suited to high-efficiency cell concepts with new contact structures. This paper describes the basic principles of this emerging interconnection technology and discusses the different material types on the market. Mechanical and electrical characterization methods for conductive adhesives are also presented. Results are included from peel tests, volume and contact resistivity measurements, metallographic investigations, dynamic mechanical analysis and differential scanning calorimetry. Finally, a novel simulation approach for the cure kinetics of ECAs and arbitrary temperature profiles is briefly described and demonstrated by an example of an epoxy adhesive cure.

Introduction

Although soldering is currently the standard interconnection technology for crystalline solar module manufacturing because of its relatively low cost and proven long-term reliability, electrically conductive adhesives (ECAs) have gained increasing attention as an alternative [1]. On the one hand, ECA is a lead-free and flux-free technology, and an adhesive can be processed at lower temperatures (120–180°C), which therefore imposes less thermomechanical stress on the cells than soldering. Moreover, ECA is usually a flexible and compliant material that can absorb and reduce mechanical stress caused by the different thermal expansion coefficients of the module components.

> "ECA is a lead-free and flux-free technology."

On the other hand, the cost of ECA is an important concern because of the high silver content in the glues that is still necessary for achieving a reasonable electrical performance. However, ECA manufacturers are currently making significant progress in driving down costs of the material, and in increasing mechanical strength while maintaining reliability. Although it has been shown by many other researchers and producers that modules fabricated with ECA can withstand IEC certification tests [2–4], there are still open questions regarding the long-term stability and degradation mechanisms of the material. The cost and the lack of long-term experience of ECA are the key factors that still limit its wider use in module manufacturing.

Despite these concerns, ECA is a key technology for emerging new high-efficiency cell concepts. The most prominent example is the metal-wrap-through (MWT) solar cell together with the module integration based on conductive backsheets [5]. MWT solar cells have both contacts on the rear side, so the busbars on the sunny side can be omitted, increasing efficiency and reducing material consumption. For the interconnection of the cells, the backsheet of the module contains a structured metal layer, comparable to a circuit board in microelectronics, where the cells are glued with ECA. The glue is cured together with the cross-linking of the encapsulation material during a standard lamination process.

Another high-performance concept comes from Sanyo, which was the first company to industrialize crystalline heterojunction solar cells and modules. The efficiency of these high-performance cells exceeds 20% [6]. Since they contain temperature-sensitive layers such as amorphous silicon and a transparent conductive oxide, the use of ECA is one possible solution for a low-temperature interconnection [7].

ECA can also be used as a substitute for the front-side busbar [8]. The busbars are omitted in the screen-printing process during solar cell fabrication, and a standard ribbon is directly glued to the grid during the interconnection process in the module fab. Eliminating the screen-printed busbar has the advantage of improved efficiency because of better passivation of the front side, but most importantly saves roughly 40% of the front-side silver paste.

This paper will begin with a brief overview of the fundamental principles of conductive adhesives. A selection of relevant characterization techniques will then be discussed. In the last section the focus will be on the cure kinetics of ECA; a modelling approach will be demonstrated, along with a presentation of the results of a simulation.

Fundamentals of conductive adhesives

Components: polymers and filler

ECAs are basically polymers that are filled with electrically conductive particles. ECAs are usually viscous pastes of monomers or pre-polymers that cross-link when they are exposed to heat to form a solid polymer. The adhesives are applied to the components by printing or dispensing techniques, and the curing is carried out by using furnaces, heating plates, thermodes or infrared lamps.

> "ECAs are basically polymers that are filled with electrically conductive particles."

The polymer matrix provides cohesion (internal strength) of the material and adhesion to the surfaces to be bonded. Interestingly, the fundamentals of adhesion are still a field of debate. Many theories exist, such as chemical bonding, physical interlocking, diffusion and physical adsorption (especially by Van der Waals forces), with the latter being the most widely accepted [9,10].

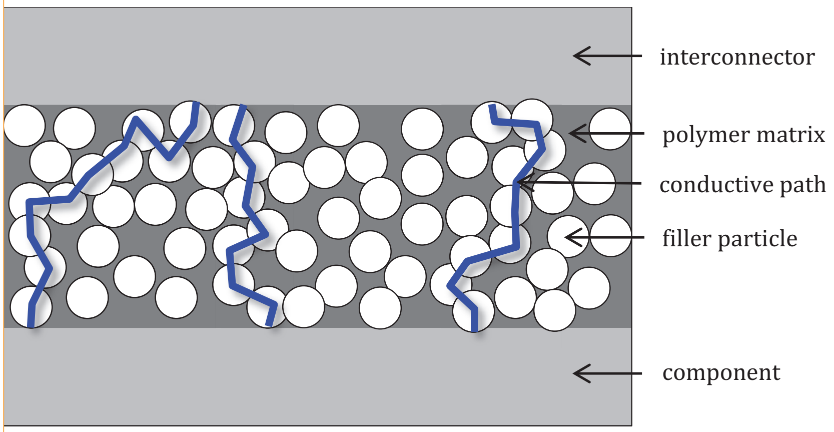

Figure 1. Schematic of a cross section of a conductive adhesive, showing how electrical paths are formed as a result of the internal contact of the filler particles.

The filler particles inside the adhesive form an electrically conductive network once the quantity is high enough to reach the so-called percolation threshold (see Fig. 1). They can be of different materials and can have various shapes and sizes, such as spheres or flakes. A 'typical' conductive adhesive is based on an epoxy polymer and contains silver flakes with 35–40 vol% and a diameter of 1–10µm. Additional components are diluting and curing agents as well as lubricants [11].

Types of conductive adhesive

Conductive adhesives for solar cell applications can be distinguished in respect of their conduction mechanism (isotropic, anisotropic) or polymer base (epoxies, acrylates, silicones).

Isotropic conductive adhesives

Isotropic conductive adhesives (ICAs) are presently the dominant type on the market. After curing, the conductivity is equally high in all directions; this is achieved by a large fraction of metal particles well above the percolation threshold. As one-component products they come pre-mixed in syringes of different sizes, frozen at –40°C. However, users also have the option to obtain the two components separately and take care of the proper mixing in their own fab, a process which requires sophisticated mixing equipment. If the user chooses the deep-frozen syringes, appropriate cooling equipment must be provided and the limited shelf life (usually six to twelve months) taken into account. Beyond expiration, particles can sink down and clog; in addition, the viscosity increases and makes the adhesives practically useless for automated equipment.

ICAs are relatively simple to process using printing or dispensing equipment and a curing step which does not require additional bonding pressure except from the fixation of the component or ribbon to the contact pad.

Anisotropic conductive adhesives

The characteristic of anisotropic conductive adhesives (ACAs) is that the current flows in one direction. Since only 0.5–5 vol% conductive particles are needed, this type of adhesive has considerable cost-saving potential.

Prominent ACAs come as conductive tapes, but paste-type products are also available. Tapes have the advantage of being clean in their application. However, they require special bonding conditions, usually at temperatures of 180°C with simultaneous pressure application of 2MPa for 10 sec [12], which may not only limit throughput but also cancel out the advantage of being a low-stress interconnection technology.

Solder-filled adhesives can also be put into this category [13]. They have the potential to be completely silver-free and almost compatible with existing module manufacturing equipment, for example a stringer used at low temperatures as a first curing step and a laminator for a final cure. Of course, modifications to the stringer are necessary in order to allow it to dispense or print the adhesive.

Epoxies

The characteristic feature of the cure reaction of epoxies is a polyaddition of components A (resin) and B (hardener) to a solid polymer. This is the most common polymer base for ECAs.

The curing time of epoxy-based ECAs ranges from 1.5 min to 10 min at 150°C. In the authors' experience, in tests the peel strength of the fully cured material is in the range of 0.2–1N/mm. Epoxies have stable properties at temperatures of up to 180–200°C and have a relatively high resistance to water and chemical attacks [14].

Acrylates

Acrylates as monomers have a particular chemical structure in that there exists a carbon–carbon double bond. This bond is cleaved by radicals during the cure reaction, resulting in the creation of new valences where the same kind of monomers can join and form the polymer network. Since only one kind of monomer is involved, the reaction is called polymerization.

The cure time at 150°C takes just a few seconds, which makes this polymer base an ideal candidate for solder replacement from a process point of view. However, acrylates are less temperature resistant, with a limitation of about 100°C [9].

Silicones

Silicones contain silicon–oxygen bonds instead of carbon chains. They are categorized as polycondensation adhesives, although silicones exist that can also be formed without the creation of a by-product.

At 150°C the cure time of silicones is in the range of 10–15 min, demonstrating a good compatibility with standard lamination times. Silicones have outstanding temperature stability, displaying high elasticity in a wide temperature range of at least –40°C to 200°C. Resistance to environmental attacks is claimed to be high [14].

Material characterization

Numerous methods are available for the mechanical and electrical characterization of conductive adhesives [15–17]. The focus here will be on the following methods: peel test, volume and contact resistance, metallography and dynamic mechanical analysis. For studying the cure reaction, the modelling procedure is based on differential scanning calorimetry experiments.

Peel test

Quality control incorporating the peel test for solar cell interconnections was reported by Wirth [18] in 2010. The foundation of the peel test is DIN EN 50461 [19]; the test was performed at a constant speed of 1mm/s and an angle of 90 degrees.

> "A major concern is the typically low peel strength of conductive adhesives compared with soldering."

A major concern expressed by industry is the typically low peel strength of conductive adhesives compared with soldering. The reason is that peel stress is a highly localized stress and adhesives are polymers with naturally lower toughness than metals, resulting in lower resistance to peeling. Moreover, adhesives are highly filled with particles that cannot contribute to the cohesive strength of the adhesive layer. Nevertheless, some adhesives, such as glue A shown in Fig. 2, are able to achieve the criterion of 1N/mm. Despite the above-mentioned drawback, other mechanical characteristics of ECAs – for example higher compliance and flexibility – may be advantageous from a long-term perspective and should not be neglected.

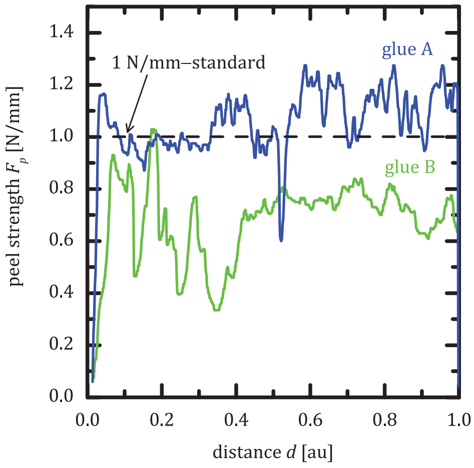

Figure 2. Peel strength of conductive adhesives.

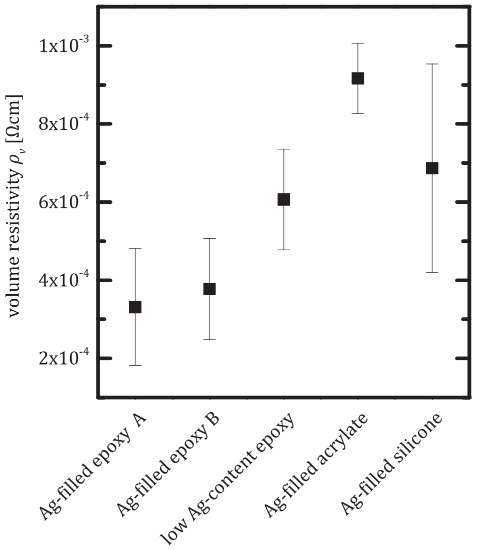

Figure 3. Volume resistivity of ECAs (error bars depict the standard deviation of the set of measurements).

Volume and contact resistivity

The volume resistance of ECAs is determined in accordance with MIL-STD-883H [20]. A cured adhesive track of defined dimensions is prepared on a glass slide. The resistance is determined by a four-point-probe measurement. The volume resistivity ρ_v can be calculated using the formula:

$$\rho_v = R_v \frac{w \cdot th}{l} \tag{1}$$

where R_v = measured resistance, w = width, th = thickness and l = length of the adhesive track.

The volume resistivity of some conductive adhesives is given in Fig. 3; it can be seen that the difference is not very distinct. Epoxies A and B are standard isotropic adhesives with ~80 wt% Ag-content and have the lowest resistance among the tested ECAs. As expected, a greater resistance can be observed for an epoxy with a low Ag content. The acrylate and silicone also have relatively high Ag contents but show higher resistances or stronger variations, which could be caused by the polymer base.

The contact resistivity of a conductive adhesive joint can be determined by the transfer length method (TLM) [21,22]. Ribbons have to be attached perpendicularly to the busbar at successively increasing distances. The resistance between adjacent contacts is determined using a four-point-measurement and then plotted against the distance. The intercept of the linear fit to the measurements with the y-axis is equal to the contact resistance R_c multiplied by two.

The contact resistivity (or specific contact resistance) can be calculated by:

$$\rho_c = R_c L_T Z \tag{2}$$

where L_T = transfer length and Z = length of the contact if a rectangular contact area is assumed.

Contact resistivities for three different glues and various ribbon coatings glued on the busbar can be seen in Fig. 4. Adhesive A is a silver-filled isotropic epoxy and works best on Ag finishes. The contact resistivity for the Ag-coated ribbon is even in the range of that corresponding to a soldered contact. It can be seen that using adhesive B on a SnAg coating leads to a contact resistance that is greater by an order of magnitude. Glue C with SnAg ribbons yields the highest contact resistivity. According to the glue manufacturer, the reason for this is that the ribbon material is not ideally suited to this type of glue.

Contact resistance is typically the dominant electrical loss factor for ECA joints and thus is of particular importance for modules built with ECA. As can be seen in Fig. 4, contact resistance strongly depends on surface metals; glue manufacturers are usually aware of which substrates the glue can be used on. In this test, initial resistance is lowest on Ag- and Cu-finished surfaces. For cost-reduction purposes it may seem reasonable to use bare Cu or Sn-coated ribbons instead of Ag, but those can lead to resistance increases due to oxidation and/or galvanic corrosion during outdoor exposure. Some adhesive manufacturers sell formulations having stable contact resistance on Sn and OSP-treated Cu, which is especially important for the MWT conductive backsheet concept that uses OSP-treated Cu circuitry on the backsheet foil.

Metallography

The inspection of cross sections by using metallographic methods gives an insight into the joint integrity

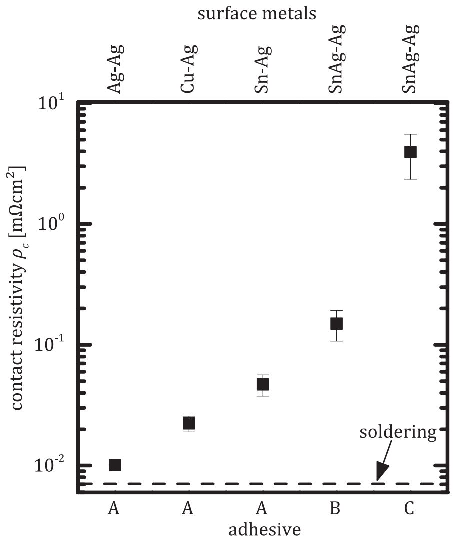

Figure 4. Contact resistivities for conductive adhesives on different ribbon coatings and front-side busbar (error bars depict the standard deviation of the set of measurements).

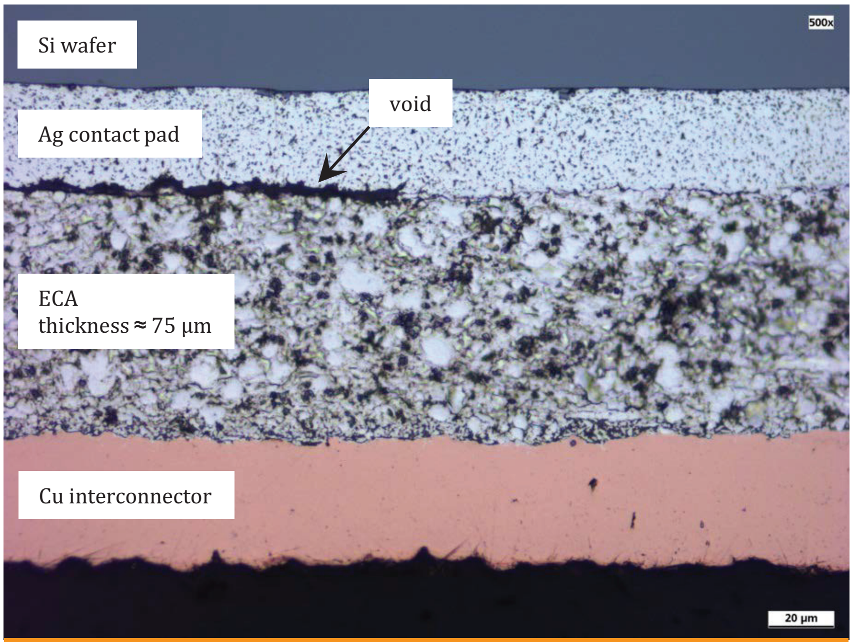

Figure 5. Cross section (500× magnification) of a conductive adhesive bond prepared with metallographic methods. A narrow void is visible between the ECA and the contact pad.

and the morphological structure of the adhesive bond. Metallographic preparation techniques require several cutting and polishing steps [23]. A polished cross section of a conductive adhesive bond of an MWT cell with a copper interconnector can be seen in Fig. 5. Important information – such as bond line thickness, voids, cracks and morphological structure of the glue – can be obtained using this technique.

Dynamic mechanical analysis

To study the mechanical bulk properties of polymers, dynamic mechanical analysis (DMA) can be used [24]. In DMA a sinusoidal force is applied to a bulk sample of an adhesive, and the resulting deformation and phase shift of the material are measured. The storage modulus E', the loss modulus E'' and the damping factor tan δ at various temperatures and frequencies can be calculated from the response. The storage modulus is a measure of the elasticity of the material, whereas the loss modulus is related to the energy that is dissipated in the bulk of the material. The damping factor is an indicator of the material's ability to lose energy through molecular rearrangements and internal friction.

> "DMA is extremely sensitive to material transitions and therefore ideally suited to studying the glass transition of ECAs."

DMA is extremely sensitive to material transitions and therefore ideally suited to studying the glass transition of ECAs. Figs. 6 and 7 show the DMA data for two different ECAs measured in tension mode at 1Hz. The glass transition temperature T_g, determined here as the peak of the tan δ curve, is considerably different for both adhesives: while the T_g of adhesive A is 31°C, for adhesive B it is 113°C. This means that adhesive A can be either soft ($E' < 1000$MPa) or rigid, depending on the operating temperature of the module. Adhesive B, however, will always be rigid within the relevant temperature range. This may give rise to concern about the reliability of the module when the mechanical properties are changing according to the temperature conditions.

Cure kinetics

Curing is an exothermal reaction, and in order to obtain kinetic information about the conductive adhesive the generated heat can be measured using differential scanning calorimetry (DSC) [25]. This method is used in polymer science primarily for investigating phase transitions, such as melting point, glass transition and crystallization.

The partial heat $Q_p(t)$ can be determined by partially integrating the heat flow, as measured by DSC, over time t. If this is then divided by the total generated heat Q_t, information about the degree of cure α over time can be obtained:

$$\alpha(t)=\frac{Q_p\,(t)}{Q_t} \qquad (3)$$

Around 15mg of a typical isotropic silver-filled epoxy was dispensed into sample pans made of aluminium, which were then hermetically sealed. Sample and reference were quickly brought to an isothermal temperature and held until the reaction was finished. Fig. 8 shows $\alpha(t)$ curves for various constant temperatures. It takes eight minutes to fully cure the adhesive at 120°C, but the reaction can be speeded up to under a minute if 170°C is used instead. The large process window and flexibility in curing conditions of most adhesives is one of the major advantages of this technology.

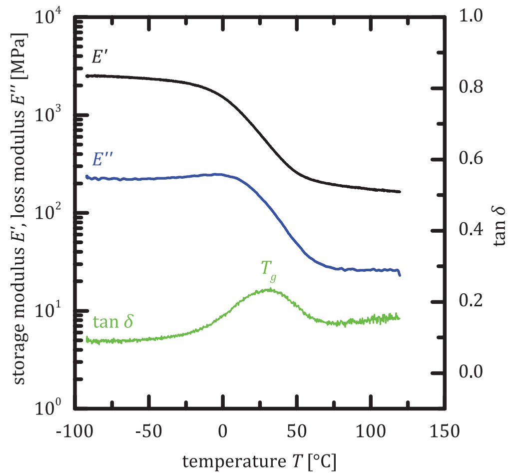

Figure 6. DMA measurement of adhesive A at 1Hz.

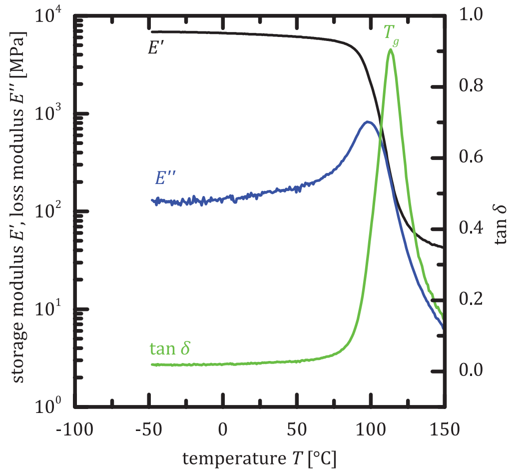

Figure 7. DMA measurement of adhesive B at 1Hz.

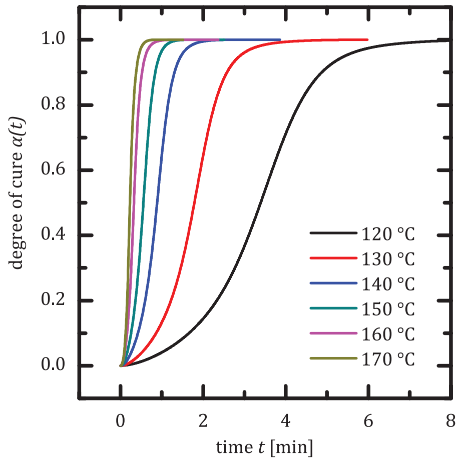

Figure 8. Degree of cure of a conductive adhesive at various constant temperatures.

> "The large process window and flexibility in curing conditions of most adhesives is one of the major advantages of this technology."

Curing is a new process step in module fabrication and having control over it is essential in order to ensure reliable interconnections. A model, along with a simulation tool to calculate the cure kinetics for an epoxy ECA and arbitrary temperature profiles, has recently been developed [26,27]. The steps are: 1) establish the model; 2) identify the model parameters with dynamic DSC measurements of the used ECA; and 3) solve the equations numerically.

The model is based on the general rate law, the Arrhenius relationship and an autocatalytic reaction model:

$$\frac{d\alpha}{dt} = Aexp\left(-\frac{E}{RT}\right)[\alpha^m(1\text{-}\alpha)^n] \qquad (4)$$

where $d\alpha/dt$ = conversion rate, A = pre-exponential factor, E = activation energy, T = absolute temperature, α = degree of cure, and m, n = exponents of the reaction model.

The task is to find values for the parameters A, E, m and n, a procedure for which has been extensively described by Geipel and Eitner [26]. Simulation results of the cure kinetics of a conductive epoxy, for example, are shown in Fig. 9. The temperature profile, represented as the dashed black line, was used as an input. The red curve shows the degree of cure, as calculated using the given temperature profile. The blue line corresponds to a simulation of an isothermal cure at 150°C; the blue squares on this curve show experimental data from the isothermal cure, highlighting the satisfactory accuracy of the model.

If the isothermal cure is compared with the temperature profile cure, one may conclude that the latter, containing an extended ramp-up phase, takes significantly longer (7 min) than the former (2 min) at comparable set temperatures. Thus, knowing the actual time needed to fully cure the adhesive is extremely helpful for process optimizations in the fab.

Conclusions

Conductive adhesives are an alternative interconnection technology well suited to high-efficiency cell concepts with new contact structures, while offering low thermomechanical stress

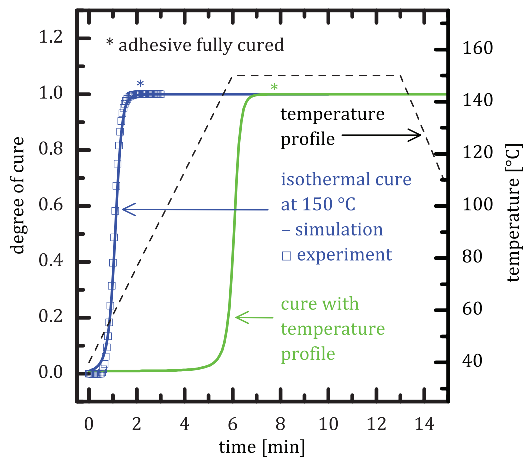

Figure 9. Simulated degree of cure with an arbitrary temperature profile, along with both simulation and experimental data of an isothermal cure at 150°C for comparison.

and high flexibility. To guarantee module reliability for 25+ years, ECAs and the involved processes have to be thoroughly understood using characterization techniques and methods common in PV and well established in polymer science.

This article has discussed a selection of mechanical and electrical methods for determining the relevant characteristics of ECAs, such as peel strength, volume and contact resistance, morphology, glass transition temperature and cure kinetics. The most important findings are summarized as follows.

It was shown that the peel strength of ECAs can reach 1N/mm; work is currently ongoing to further improve this.

The electrical losses of ECA bonds are dominated by contact resistivity, and particular attention must be given to the compatibility of the surface metals. Ag demonstrated the lowest resistivity of typically 0.01–0.1mΩcm^2, which is in the range of that of a soldered contact. Cu, Sn and SnAg yielded significantly higher resistivities (> 0.1mΩcm^2), and the compatibility with an adhesive must be investigated for each specific case. However, if not protected from moisture, all non-noble metals – Sn and Cu for example – during long-term testing are prone to oxidation and/or galvanic corrosion, which can dramatically increase the resistance.

By metallographic investigations it was observed that the most common filler shapes are flakes and spheres with a diameter of 1–10µm. Moreover, the existence of voids is a concern in terms of the adhesive bond quality having an impact on mechanical and electrical performance losses.

Additionally, DMA measurements were carried out in order to investigate the bulk properties of adhesives. Wide variations in glass transition temperature were seen among the adhesives. An interesting question for further discourse is how these differences in mechanical characteristics with regard to the module's operating temperature range can affect reliability.

> "ECA is a technically interesting, reliable and even cost-competitive interconnection technology for high-efficiency solar modules."

Finally, a model was established and used to simulate the degree of cure over time for any given temperature profile for an epoxy ECA. The actual curing time using a specific heating device is usually longer than that for an ideal isothermal cure at a comparable set temperature. In the authors' opinion, ECA is a technically interesting, reliable and even cost-competitive interconnection technology for high-efficiency solar modules.

References

[1] Beier, B. et al. 2001, "Electrical conductive adhesives: A novel reliable method for interconnecting crystalline silicon solar cells", *Proc. 17th EU PVSEC*, Munich, Germany, pp. 812–815.

[2] Bennett, I. et al. 2007, "Low-stress interconnection of solar cells", *Proc. 22nd EU PVSEC*, Milan, Italy, pp. 2674–2678.

[3] Späth, M. et al. 2011, "Hetero-junction module technology", *Proc. 26th EU PVSEC*, Hamburg, Germany, pp. 3121–3124.

[4] Zemen, Y. et al. 2011, "Innovative and gentle interconnection technique for high efficiency c-Si solar cells and cost-of-ownership-analysis (COO)", *Proc. 26th EU PVSEC*, Hamburg, Germany, pp. 3125–3132.

[5] Lamers, M. et al. 2012, "17.9% Metal-wrap-through mc-Si cells resulting in module efficiency of 17.0%", *Prog. Photovolt.: Res. Appl.*, Vol. 20, No. 1, pp. 62–73.

[6] Mishima, T. et al. 2011, "Development status of high-efficiency HIT solar cells", *Solar Energy Mater. & Solar Cells*, Vol. 95, No. 1, pp. 18–21.

[7] Scherff, M.L.D. et al. 2006, "10 × 10 cm^2 HIT solar sells contacted with lead-free electrical conductive adhesives to solar cell interconnectors", *Proc. 4th IEEE WCPEC*, Waikoloa, Hawaii, USA, pp. 1384–1387

[8] Schneider, A. et al. 2012, "Conductive gluing as interconnection technique towards solar cells without front busbars and rear pads", *Proc. 27th EU PVSEC*, Frankfurt, Germany, pp. 335–339.

[9] Adams, R.D. (Ed.) 2005, *Adhesive Bonding: Science, Technology and Applications*, Cambridge: Woodhead Publishing Limited.

[10] Habenicht, G. 2009, *Kleben: Grundlagen, Technologien, Anwendungen*, Berlin, Heidelberg: Springer.

[11] Chunduri, S.K. 2011, "Sticky and cool", *Photon International*, No. 11, pp. 158–165.

[12] Kopeček, R. et al. 2010, "Aluminium rear emitter large area n-type Cz-Si solar cells for industrial application", *Proc. 25th EU PVSEC*, Valencia, Spain, pp. 2381–2386.

[13] Eom, Y.-S. et al. 2010, "Electrical interconnection with a smart ACA composed of fluxing polymer and solder powder", *ETRI J.*, Vol. 32, No. 3, pp. 414–421.

[14] Habenicht, G. 2008, *Kleben - erfolgreich und fehlerfrei: Handwerk, Praktiker, Ausbildung, Industrie*, Wiesbaden: Vieweg+Teubner.

[15] Eitner, U. et al. 2012, "Characterization of electrically conductive adhesives", *Energy Procedia*, Vol. 27, pp. 676–679.

[16] Hinz, I. et al. 2012, "Characterization of electrical conductive adhesives (ECA) for the photovoltaic-industry", *Proc. 27th EU PVSEC*, Frankfurt, Germany,

pp. 3474–3478

[17] Li, Y., Wong, C. & Lu, D. 2009, “Characterizations of electrically conductive adhesives”, in *Electrical Conductive Adhesives with Nanotechnologies*, New York, Dordrecht, Heidelberg, London: Springer, pp. 81–120.

[18] Wirth, H. 2010, “Tabbing-stringing quality control challenges”, *Photovoltaics International*, 9th edn.

[19] DIN 2007, “Solar Cells – Datasheet information and product data for crystalline silicon solar cells”, DIN EN 50461.

[20] U.S. Department of Defense 2010, “Test Method Standard – Microcircuits”, MIL-STD-883H.

[21] Berger, H.H. 1972, “Contact resistance and contact resistivity”, *J. Electrochem. Soc.*, Vol. 119, No. 4, pp. 507–514.

[22] Schroder, D.K. 2006, “Contact resistance and Schottky barriers”, in *Semiconductor Material and Device Characterization*, Hoboken, New Jersey: John Wiley & Sons, pp. 127–184.

[23] Eberlein, D., Schmitt, P. & Voos, P. 2011, “Metallographic sample preparation of soldered solar cells”, *Practical Metallography*, Vol. 48, No. 5, pp. 239–260.

[24] Menard, K.P. 2008, *Dynamic Mechanical Analysis: A practical introduction*, Boca Raton, London, New York: CRC Press.

[25] Li, L. & Morris, J.E. 1999, “Curing of isotropic electrically conductive adhesives”, in *Conductive Adhesives for Electronics Packaging*, Port Erin, Isle of Man: Electrochemical Publications Ltd., pp. 99–116.

[26] Geipel, T. & Eitner, U. 2013, “Cure kinetics of electrically conductive adhesives for solar cell interconnection”, *IEEE J. Photovolt.*, Vol. 3, No. 4.

[27] Geipel, T. & Eitner, U. 2013, “Cure kinetics of electrically conductive adhesives”, *Energy Procedia* [forthcoming].

About the Authors

Torsten Geipel received the Diploma degree in information system technology from the Technical University of Dresden in Germany. His diploma thesis concerned 2D simulation methods for silicon solar cells. From 2008 to 2011 Torsten worked on cell and module characterization and reliability testing in the Department of Research and Development at the module and system manufacturer Solon SE in Berlin. He joined the Photovoltaic Modules group at Fraunhofer ISE in November 2011 as a doctoral student, studying electrically conductive adhesives.

Ulrich Eitner studied technical mathematics at the University of Karlsruhe (TH). From 2006 to 2011 he worked in the field of thermomechanics of PV modules at the Institute for Solar Energy Research Hamelin (ISFH) and obtained his Ph.D. from the University of Halle-Wittenberg in 2011. Dr. Eitner has been managing the Photovoltaic Modules group at Fraunhofer ISE since 2011.

Enquiries

Torsten Geipel
Fraunhofer Institute for Solar Energy Systems ISE
Heidenhofstrasse 2
79110 Freiburg
Germany

Tel: +49 761 45885023
Email: torsten.geipel@ise.fraunhofer.de
Website: www.ise.fraunhofer.de