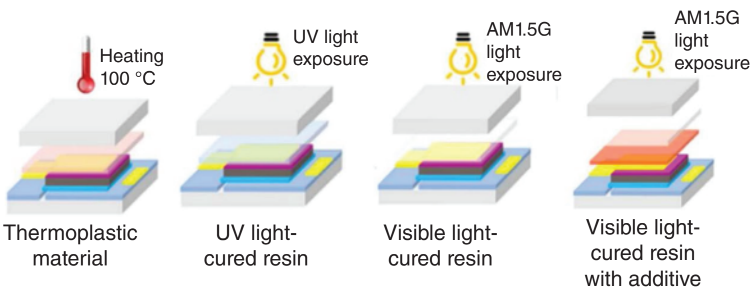

Figure 1.31 Several operating conditions for the preparation of polymeric encapsulation layers. Source: Reproduced with permission from Shi et al. [41]; © 2020, American Association for the Advancement of Science.

large-area encapsulation. Common materials used for encapsulation include polyisobutylene, PE, thermoplastic polyurethane, EVA, and cyclized perfluoropolymers. Various preparation methods for encapsulation layers are available, such as thermal curing, UV curing, and visible light curing, as shown in Figure 1.31 [41].

Recently, Dr. Lei Shi from the Australian Centre for Advanced Photovoltaics and Prof. Anita Ho-Baillie from the University of Sydney [40] investigated the encapsulated chalcogenide solar cell system using gas chromatography–mass spectrometry (GC–MS) and found that the polymer-glass "blanket-cover" encapsulation technique can form an absolutely hermetic system and greatly improve the operating life of chalcogenide solar cells. The polymer-glass encapsulation technique allows the efficiency of chalcogenide solar cells to remain above 95% after 4000 hours of operation under IEC 61215:2016 standard test conditions. The (GC–MS) technique reveals that the absolute hermetic encapsulation effectively prevents the diffusion of various decomposition gas molecules and maintains the equilibrium of the system, and the residual vapor can promote the regeneration of chalcogenide at night, which increases the cycle life of the cell. The "blanket" encapsulation technique, in which the entire device is encapsulated with a polymer so that the device is in close contact with the polymer and there are no cavities inside. Interestingly, the authors added a layer of Cover Glass to the encapsulated cell, which effectively prevents the escape of CH_3Br and NH_3 from the decomposition of chalcogenide, an effect that cannot be achieved with polymer encapsulation alone. The polymer acts not only as a water vapor barrier but also as a strong binder between the chalcogenide solar cell and the cover glass, further enhancing the hermetic performance of the system (Figure 1.32).

For the encapsulation of calcium titanite solar cells, the researchers employed polyisobutylene and polyolefin. They subjected the cells to hygrothermal and humidity freeze tests within a temperature range of −40 to 80 °C. Remarkably, the cells encapsulated with this technique showed no degradation after 1800 hours of operation, surpassing the 1000-hour requirement stipulated in the test standard. The short-circuit current density and open-circuit voltage of the cells remained stable even after the test, a characteristic commonly observed in calcium titanite solar cells containing methylamine ions.

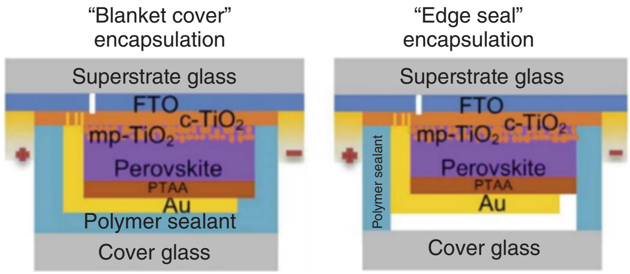

Figure 1.32 Cross-sectional diagram of "blanket cover" and "edge seal" encapsulations. Source: Reproduced with permission from Juarez-Perez and Haro [40]; © 2020, American Association for the Advancement of Science.

This study demonstrates that the use of simple and cost-effective polymer-glass combination encapsulation techniques, such as polyisobutylene or polyolefin-based encapsulation, can confer exceptional durability to organic–inorganic hybrid chalcogenide solar cells. Notably, these cells exhibited remarkable resilience against severe humidity freeze tests, despite the known low thermal stability of methylammonium ions, which has typically been a challenge in achieving highly stable chalcogenide solar cells. The polymer-glass "blanket-cap" encapsulation technology ensures absolute hermeticity, creating a stable operating environment that prevents decomposition products from escaping the system and significantly extending the lifespan of chalcogenide solar cells. This work offers new insights for designing more stable chalcogenide solar cells and greatly advances the commercialization of this technology [40].

1.4 Flexible Electronic Encapsulating Materials

1.4.1 Selection Principle of Flexible Electronic Encapsulating Materials

Flexible electronic encapsulating materials are utilized to support and protect flexible electronic devices, as well as establish interconnections between devices and external circuits. They play multiple roles, including mechanical support, environmental sealing, signal transmission, heat dissipation, and shielding. These materials consist of substrates, wiring, frames, interlayer media, sealing materials, and more. Among them, flexible electronic encapsulating substrate materials primarily provide mechanical support and airtight protection and facilitate heat dissipation for flexible electronic devices and their interconnections.

The selection of flexible electronic encapsulating materials should consider the following aspects:

(1) **Thermal expansion coefficient**: Matching the thermal expansion characteristics of the substrate and flexible electronic devices
(2) **Dielectric properties (permittivity and loss)**: Ensuring fast response and minimal delay in electrical signal transmission within the circuit

(3) **Thermal conductivity**: Facilitating heat dissipation from the working circuit
(4) **Mechanical properties**: Possessing adequate strength, hardness, and toughness.

Flexible electronic encapsulating substrate materials are commonly composed of plastic encapsulating materials, typically thermosetting materials such as epoxy, caseinate, polyester, and silicone. Among these, epoxy resin is the most widely used. Plastic encapsulating materials are popular in the electronic encapsulation industry due to their low cost, maturity, and simple production processes. However, they also have notable drawbacks. Most plastic materials lack sufficient density, exhibit poor thermal conductivity, possess thermal expansion coefficients that do not match flexible electronic devices, have high dielectric loss, and tend to be brittle. Plastic encapsulating materials are susceptible to moisture absorption, which leads to expansion and the potential for device failure, particularly with epoxy materials being highly affected by moisture. This significantly impacts the reliability of encapsulation, making them unsuitable for industries with higher reliability requirements, such as military and aerospace. Through ongoing research on encapsulating materials, these issues can be effectively mitigated by adjusting the ratio of plastic encapsulating materials and optimizing processing methods. Ideally, plastic encapsulating materials should possess the following characteristics: high raw material purity, low viscosity, minimal impurities, low water absorption, good heat resistance, high thermal conductivity, matching thermal expansion coefficients, ease of processing and molding, minimal raw material waste, good flame retardant properties, and excellent environmental performance without toxicity or pollution.

1.4.2 Desirable Properties of Flexible Electronic Encapsulating Materials

To minimize the impact of environmental factors such as water, oxygen, and dust on flexible electronic devices, flexible electronic encapsulating materials must meet the performance requirements specified in national standards. General performance indicators include insulation, breakdown strength, heat resistance, mechanical strength, and WVTR.

(1) **Insulation**: Flexible electronic encapsulating materials should exhibit high insulation resistance, typically exceeding 30 MΩ under normal conditions.
(2) **Breakdown strength**: When the electric field strength exceeds a certain threshold, flexible electronic encapsulating materials may experience a breakdown, leading to a loss of insulation properties. Generally, the breakdown strength requirement for flexible electronic encapsulating materials is above 10 KV/mm.
(3) **Heat resistance**: With increasing temperature, the resistance, breakdown strength, and mechanical strength of flexible electronic encapsulating materials tend to decrease. Therefore, flexible electronic encapsulating materials should maintain stable and reliable insulation and sealing performance while operating within specified temperature ranges for extended periods.

(4) **Mechanical strength**: Depending on specific requirements, different mechanical strength indicators such as tensile strength, compressive strength, bending strength, shear strength, tear strength, and impact resistance may be specified for different flexible electronic encapsulating materials.
(5) **Water and oxygen transmission rates**: Water and oxygen transmission rates, including WVTR and oxygen transmission rate, are measured in grams per square meter per day ($g/m^2/day$) and cubic centimeters per square meter per day ($cm^3/m^2/day$), respectively. As water vapor molecules are smaller than oxygen molecules and are more difficult to block, the WVTR is used to evaluate the encapsulation's effectiveness. The WVTR indicates the weight of water vapor that passes through a unit area of material under specific time, temperature, and humidity conditions. The oxygen transmission rate, on the other hand, measures the volume of oxygen that permeates through a unit area of material within a given time under constant temperature and pressure differences. Typically, flexible electronic encapsulating devices require a WVTR below 10^{-6} $g/m^2/day$ and an oxygen transmission rate below 10^{-5} $cm^3/m^2/day$.
(6) **Other characteristics**: Certain flexible electronic encapsulating materials may exist in liquid form, such as various resins. Their properties include viscosity, fixed content, acid value, drying time, curing time, and more. Additional characteristics of flexible electronic encapsulating materials may encompass permeability, oil resistance, elongation, shrinkage, solvent resistance, arc resistance, and others.

1.5 Overview of the Development of Flexible Electronic Packaging at Home and Abroad

The development of flexible electronic packaging has seen significant progress both domestically and internationally. Currently, Japanese companies such as Sumitomo Chemical, Shin Kong Electric, Toppan, Tanaka, and Mitsui High-tec hold a substantial market share of around 25% globally. DuPont, a global leader in fluorine material development and production, is also a key player in the future competitive landscape of electronic encapsulating materials, with its market share steadily expanding. DuPont's involvement in the field has provided new development ideas for other fluorine material companies. Given the numerous advantages of fluorine materials and their experience in fluorine encapsulating technology, it is anticipated that fluorine materials will play a significant role in the field of flexible electronic encapsulation.

China represents the main application market for flexible electronic encapsulating materials, accounting for approximately 40% of the global market demand, followed by the United States with a share of around 15%. However, China currently lacks well-known enterprises focused on the development and production of functional materials in the field of flexible electronic encapsulating, unlike DuPont and Sumitomo Chemical. Although domestic fluorine chemical giants such as Juhua and San Aifu have shown interest in this area, they are still in the initial stages and cannot yet compete with international giants like DuPont. Therefore, flexible electronic encapsulating materials could be another area where foreign companies have a competitive advantage over domestic ones.

The global encapsulating industry has experienced single-digit growth, with statistics indicating that Taiwan accounts for 53% of sales, occupying half of the global encapsulating industry. Mainland China and the United States follow with shares of 21% and 15%, respectively, ranking second and third. Malaysia, South Korea, Singapore, and Japan each hold shares of 4%, 3%, 2%, and 2%, respectively. In terms of market share, domestic encapsulating companies have entered the global top tier and possess a certain level of international competitiveness.

Over the next five years, the competition pattern in the electronic encapsulating materials market is expected to be established. Leading global companies in this field include DuPont, Evonik, EPM, Mitsubishi Chemical, Sumitomo Chemical, Mitsui High-tech, Tanaka, Shin Kong Electric, Panasonic, Hitachi Chemical, Kyocera Chemical, Gore, BASF, Henkel, AMETEK Electronics, Toray, Maruwa, Lida Fine Ceramics, NCI, Chaozhou Sanhuan, Nippon Micrometallic, Toppan, Dainippon Printing, Germany Posel, and Ningbo Kangqiang, among others. Various authorities predict that the global electronics encapsulating market will experience rapid growth with a stunning CAGR from 2023 to 2028.

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