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PHOTOVOLTAICS: APPLICATIONS OF
SURFACE ANALYSIS AND
MOLECULAR BEAM EPITAXY

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The future of photovoltaics as a viable energy alternative still depends largely upon the improvement of solar cell performance, the reduction of most of the inherent system costs, and the establishment of device and array reliability for reasonable lifetimes (e.g., 10 to 20 years). At present, no device technology presents a clear choice and much R&D remains to be done before a decision can be made. Some predictions, however, can be made in view of the goals of the National Photovoltaic Program [1] and the economics of solar cell technology. In the near term, the only commercialized solar cell array - the flat-plate single-crystal silicon array - and possibly some low concentrator arrays (again based upon single-crystal silicon) appear as the only choices for remote, rural, foreign, and federal markets [2]. In the mid- to long-term (i.e., beyond 1986), less expensive photovoltaic alternatives, none of which are currently available commercially, are needed [3]. Most commonly mentioned among these are (1) the less expensive, intermediate efficiency (>10%) thin-film or multicrystalline solar cells; and (2) the more expensive, very high efficiency (>30%) single-crystal, high concentration solar cells [3]. The thin-film or multicrystalline solar cell provides lower cell cost through a combination of lower material utilization, less-pure starting materials, less-perfect cell materials and structures, and utilization of less energy-intensive, large-scale production methods. The single-crystal cell is more complicated. It involves the stacking of junctions in a single integrated structure in which each junction is designed to respond to a different region of the solar spectrum, thus making a more comprehensive use of the available solar energy. In this high concentration situation (about 1000 suns), the support, tracking, and optics costs of the concentrator system are quite high and the relatively high cost of the solar cell does not significantly affect overall array costs [3]. However, whether one considers the near-, mid-, or long-range solutions, it is evident that a good amount of surface and interface analysis is and will be necessary to understand and improve device performance as well as to uncover the mechanisms which cause the degradation of these photovoltaic devices. In addition, the evolution of controlled material growth techniques can have a significant effect on the development of very high efficiency cells and the understanding of the basic mechanisms involved in polycrystalline devices. The application of surface analysis methods and controlled growth techniques to photovoltaic device technology is the subject of this article.

Applications of Surface Analysis to Photovoltaics

Quite simply, photovoltaic device performance depends upon both the composition of the materials and, especially, the integrity of the numerous interfaces between the material layers. Figure 1 shows a simplified cross section of a thin-film device. The major device interfaces are the grid or upper-contact/semiconductor interface (A), the semiconductor/semiconductor (or junction) interface (B), and the semiconductor/back-contact region (C). For the polycrystalline device, these interfaces can be complicated by the intersection of grain boundaries (A', B', and C'), where enhanced interactions can occur. Additional interfaces are the antireflective coating (ARC) interface with the semiconductor surface, the interface with the encapsulation (either a glass or a polymer), and the interfaces of the top or bottom contacts with the soldered or bonded wire lead. The consideration and examination of all these complicated material interfaces can produce some skepticism about device reliability in even the most ardent photovoltaics advocate. This is especially true if one considers the exposure to severe fields, changing loads, illumination levels, temperature gradients, and the entire processing sequence that the device must endure. These problems, however, must be confronted by the photovoltaic scientist/engineer, and they provide some interesting challenges for the surface analyst.

The major problems encountered in photovoltaic devices are similar to those of other semiconductor device technologies except that the problems are compounded by the

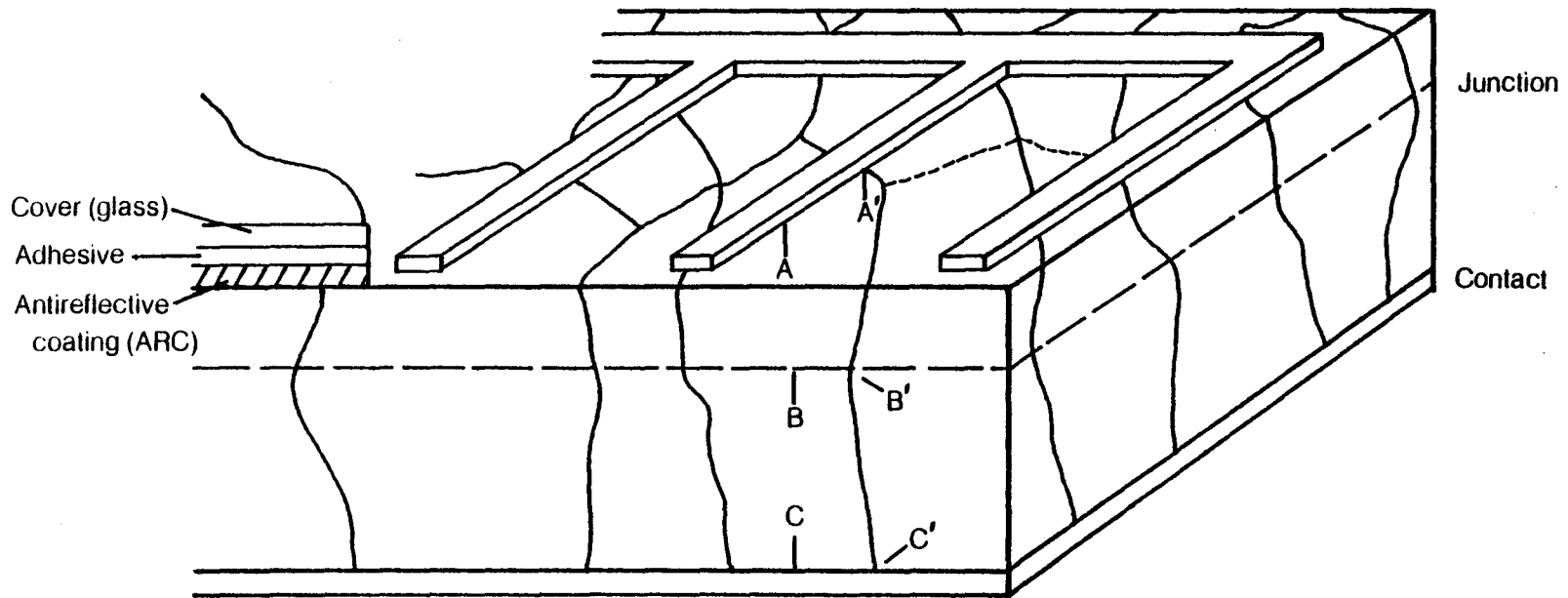


Figure 1. Schematic representation of thin-film polycrystalline photovoltaic device.

large areas of the devices (1 to 100 cm²) and the many environmentally induced degradation (i.e., due to humidity, temperature, photochemistry, and variable stresses). Three major problems resulting from either the fabrication procedures or the deployed conditions are:

- diffusion problems (interdiffusion, grain boundary diffusion, ion migration, impurity segregation),
- chemical reactions (corrosion, chemical states and changes), and
- contamination (interface, surface and trace impurities).

Although each surface analysis technique can contribute to the solution of one or more of these problems, combinations of two or more of these techniques [usually Auger electron spectroscopy (AES), secondary ion mass spectroscopy (SIMS), ultraviolet photoelectron spectroscopy (UPS), ion scattering spectroscopy (ISS), and electron spectroscopy for chemical analysis (ESCA), and their variations] provide more dependable and unambiguous results. Numerous examples of such applications are cited in the literature. It is beyond the space limitations of this review to examine all of them, but some representative examples and probable research areas are briefly indicated.

The effects of interdiffusion upon the performance and stability of solar cells become more significant as the device and layer thicknesses decrease. While a 500- to 1000-Å interdiffused region at a metal semiconductor contact might have little effect on the electrical characteristics of a 0.5-mm-thick single-crystal silicon solar cell, it would severely limit the performance of a Cu₂S/CdS thin-film heterojunction having a 1500- to 2000-Å Cu₂S semiconductor layer. In fact, in the case of polycrystalline materials the diffusion can be greatly enhanced at the grain boundary (i.e., diffusion coefficients three to six orders of magnitude higher), thus providing a mechanism for device failure.

The applications of several surface analysis techniques to the detection and solution of performance-limiting and degradative problems in solar cells are reviewed in the literature [4]. Representative cases can be found for both single-crystal and polycrystalline cell types. Of the various junctions, including homojunctions, heterojunctions, metal/semiconductor (Schottky barrier) and metal-oxide/semiconductor junctions, and electrochemical (semiconductor/liquid junctions) cells, none are exempt from surface/interface problems and all can benefit from the knowledge that careful surface analysis can produce.

Several worthwhile research areas can be noted. An example is the Cu₂S/CdS thin-film solar cell, which is the highest efficiency (9.15%) true thin-film device produced to date [5]. The conversion performance of this device shows steady improvement, but much remains unknown about its stability. Although the Cu₂S surface is reported to be extremely oxygen sensitive, carefully controlled experiments (perhaps using high-resolution ESCA) are needed to examine the microstructure response of the material and cell to oxidation and reduction treatments. The results could have significant effects on the complexity and expense of the encapsulant needed for these devices. The mechanisms of Cu migration are still under investigation. ESCA, SIMS, and scanning auger microprobe (SAM) analyses are needed in conjunction with voltage, thermal, and illumination stress tests to sort out and ascertain the extent of interdiffusion, grain boundary diffusion, electrolytic decomposition, and photoelectrochemical effects. Many of these problems apply also to other device types.

An interesting role that surface analysis can play is in the development of new and perhaps less expensive materials. The present cost of the material used in the single-crystal silicon solar cell is about six times too high. Recently, devices with efficiencies in the 15% range have been fabricated from multicrystalline silicon [6]. This material is produced by a special casting process similar to that used in casting steel and it has grain sizes in the 2- to 10-mm range. Three positive features of this material are: (1) reported efficiencies of devices fabricated from this material are close to those of single crystal cells; (2) the casting process promises to be less energy intensive than the single-crystal growth (Czochralski) technique; and (3) there are some indications that less pure (and less expensive) starting material can be used in the casting process. It is in the third area that surface analysis can be useful.

SAM and SIMS have been used in conjunction with *in situ* (ultrahigh vacuum) fracturing of multicrystalline silicon to examine the localization of impurities resulting from the casting process. Figure 2 shows a SED micrograph of a grain boundary region exposed by the UHV fracturing procedure, indicating several obvious inhomogeneous regions. Auger mapping is used to show the localization of Ni, Al, and C at the grain boundary. In addition, oxygen seems prevalent over the entire grain boundary area. Since some of the impurities of interest are beyond the detectability limits of AES, SIMS analysis of the fractured region was performed. An oxygen leak is used to enhance the secondary ion yields. For regions which are fractured through a grain, the SIMS spectra indicate only the presence of silicon; there are very few impurities (see Fig. 3). The oxides result from the oxygen leak, and the Na and K result from the inevitable inclusion of the top and bottom surfaces of the thin samples in the SIMS process. In contrast, many impurities are observed in fractures at the grain boundary (see Fig. 4). It has been proposed that the casting process fosters the migration of such impurities to the grain boundary regions. Although some of these impurities would have a devastating effect on the performance of a normal single-crystal device, their combination and migration to the grain boundary have a passivating effect on these regions in multicrystalline cast material.

The potential of surface analysis in the photovoltaics area is massive. The contributions and experiments await the ingenuity of the surface/interface researcher.

Molecular Beam Epitaxy and Photovoltaics

Molecular beam epitaxy (MBE) is a rapidly developing growth technique that has two major advantages for device researchers: (1) thin semiconductor layers can be reproducibly grown with precise doping profiles; and (2) the processing is usually done at lower-than-normal temperatures, allowing the preparation of abrupt controlled interfaces in the devices. The major uses of MBE for photovoltaics are still confined to the research area and can be generally categorized into two applications:

- diagnostic fabrication of (polycrystalline) thin-film devices, and
- demonstration/fabrication of very high efficiency devices.

It is not yet apparent that MBE can provide the large-scale, large-area production capabilities that are envisioned for photovoltaics, but in the near term it can provide important scientific information which can be used to demonstrate the feasibility of particular photovoltaics approaches.

Diagnostic fabrication of thin-film devices is not an intended use for this epitaxial growth technique; the chief strength of MBE is in producing very perfect crystalline

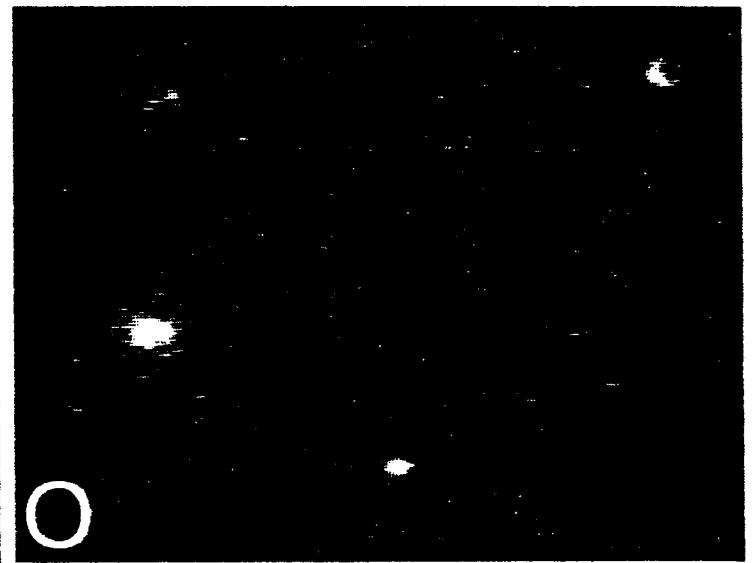
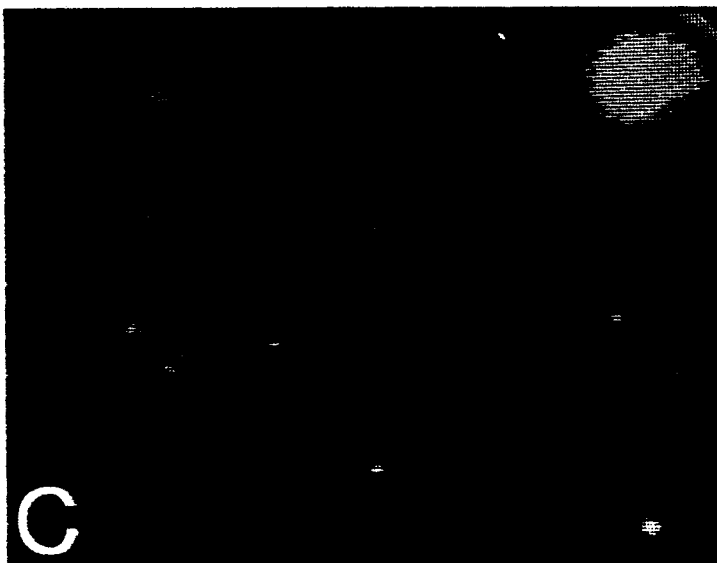
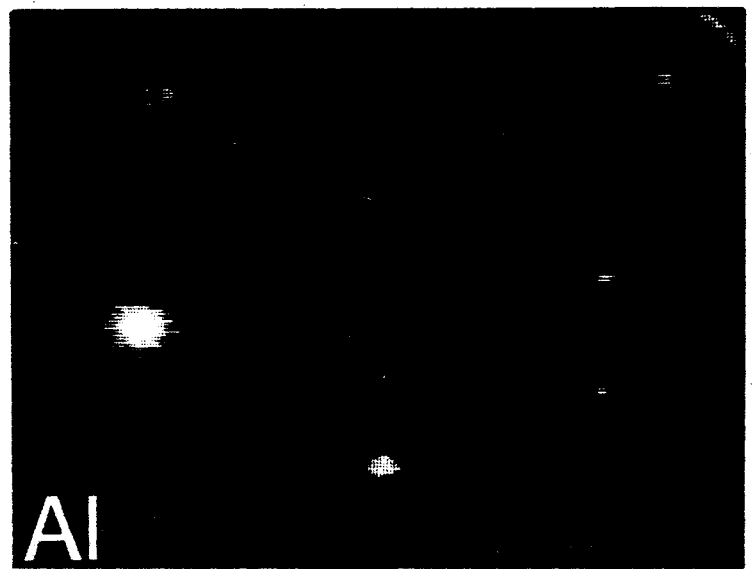
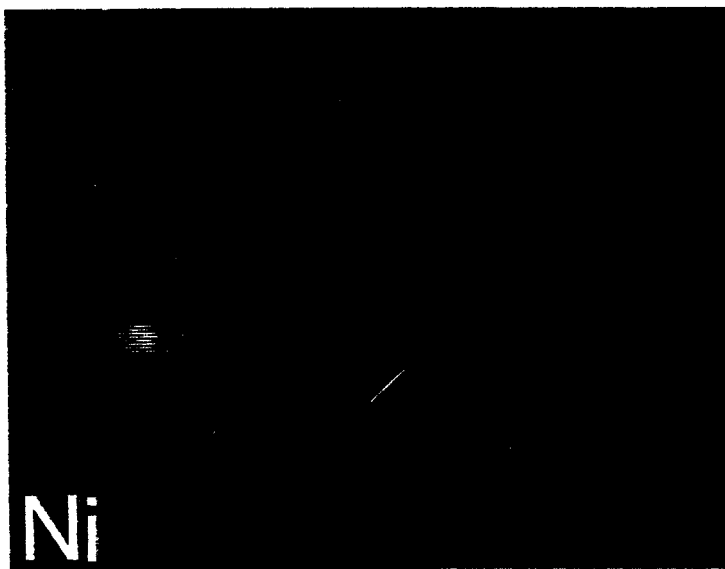
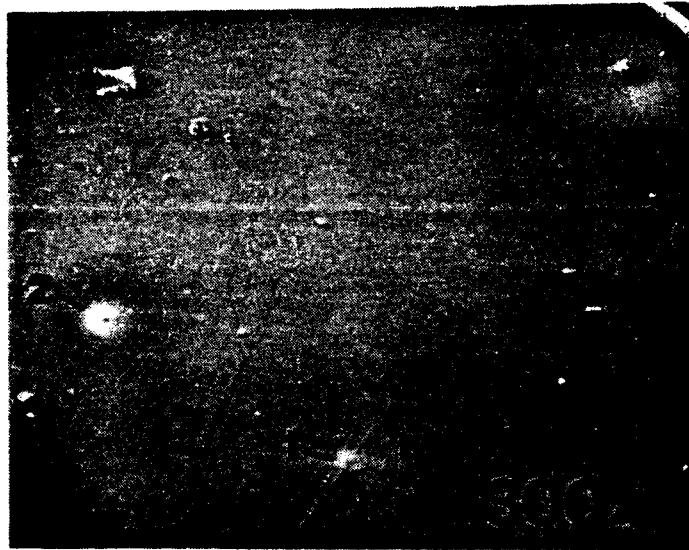


Figure 2. (a) A secondary electron image of a grain boundary region in a fractured multicrystalline silicon photovoltaic device, with (b) Ni, (c) Al, and (d) C images showing localization at the grain boundary; (e) O is prevalent over the entire area.

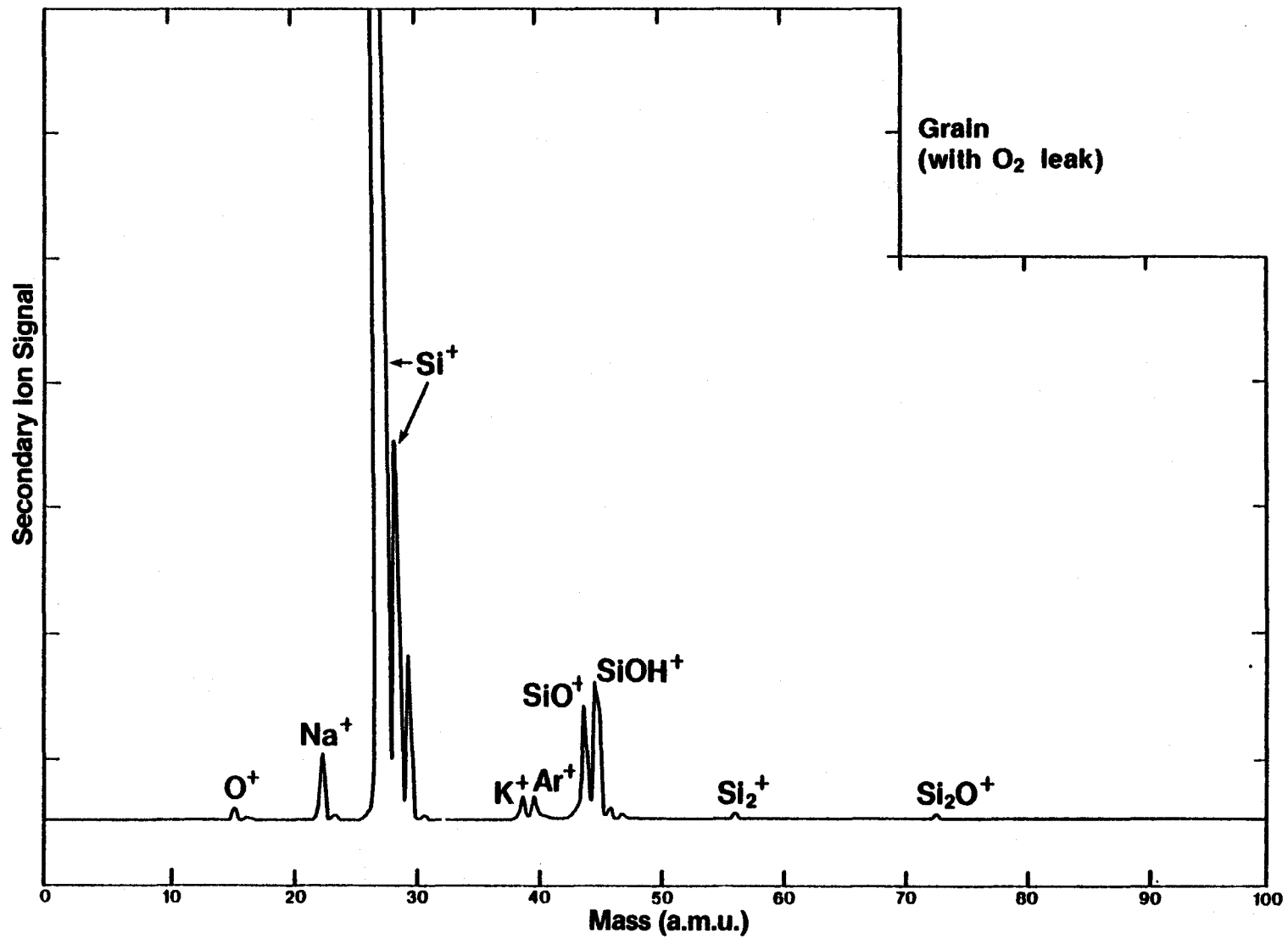


Figure 3. SIMS spectrum of a multicrystalline silicon photovoltaic device.

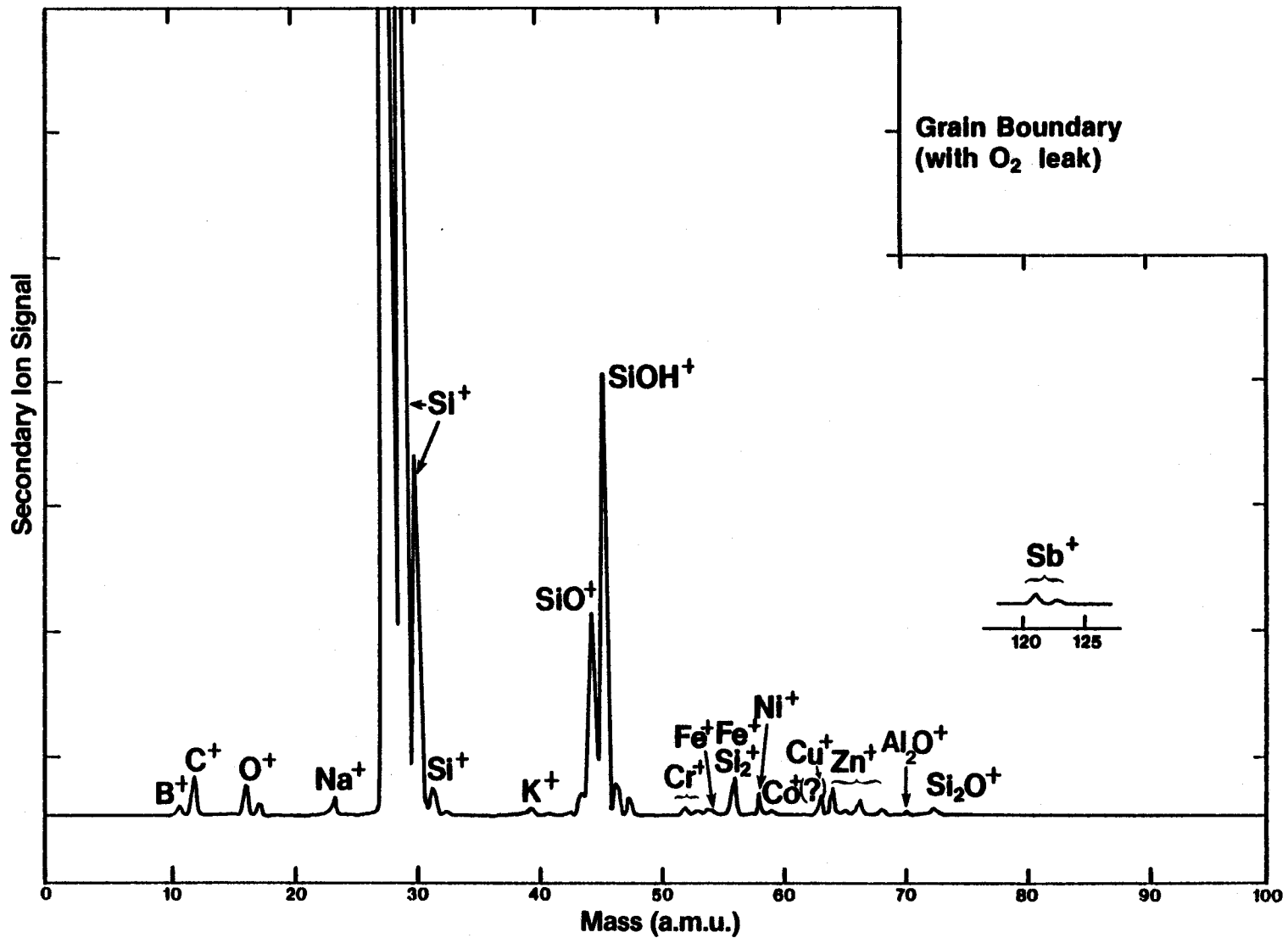


Figure 4. SIMS spectrum of a grain boundary region on the surface of a fractured multicrystalline silicon photovoltaic device.

layers. However, because of the range of parameters involved in the process and the precise control the operator has of them, MBE can be used as a diagnostic fabrication technique. In the development of thin-film solar cells, MBE provides an ideal method for varying the degree of polycrystallinity (small grain sizes to single-crystal films), changing the interface properties (doping, lattice matching), and investigating the effects of controlled impurity levels and layer thicknesses. Each of these important variables can be directly correlated with its effect on device performance, providing valuable input to solar cell design. MBE also promises to provide a method for experimentally verifying attainable (not theoretical) efficiencies for these photovoltaic devices. Thus, even though the MBE method might not be the mass production technology for thin-film solar cells, it could be instrumental during the decision process regarding which device types should be further developed.

The second application for MBE is currently receiving serious attention: the production and demonstration of very high efficiency (greater than 30%) solar cells. As previously mentioned, this long-term option probably requires the fabrication of a multilayered integrated structure. Such a two-junction device is shown in Fig. 5. The rather severe constraints on the design and fabrication of this more complex solar cell are apparently matched by the precision and control provided by MBE. For instance, the material used in the makeup of such a device must be nearly lattice matched to maintain crystal integrity and avoid interface losses. Second, the band gaps of the materials must be precisely adjusted to match effectively the entire solar spectrum. Third, the layer thicknesses have to be precisely controlled to provide current continuity in the structure. Fourth, the growth temperature should be as low as possible to minimize interdiffusion problems. Finally, a low series resistance connection must be provided between the junctions to avoid unacceptable voltage losses. (One approach to the resistance problem is to provide a tunnel junction, shown in Fig. 5, which needs very high doping.) MBE can meet these technical problems and allow the demonstration of the feasibility of a two-junction device.

Photovoltaics is an expanding area of research. The problems present challenges to device and materials scientists in general. However, surface scientist/engineers and researchers involved in specialized growth techniques are most important in the realization of photovoltaic energy conversion as a large-scale energy alternative.

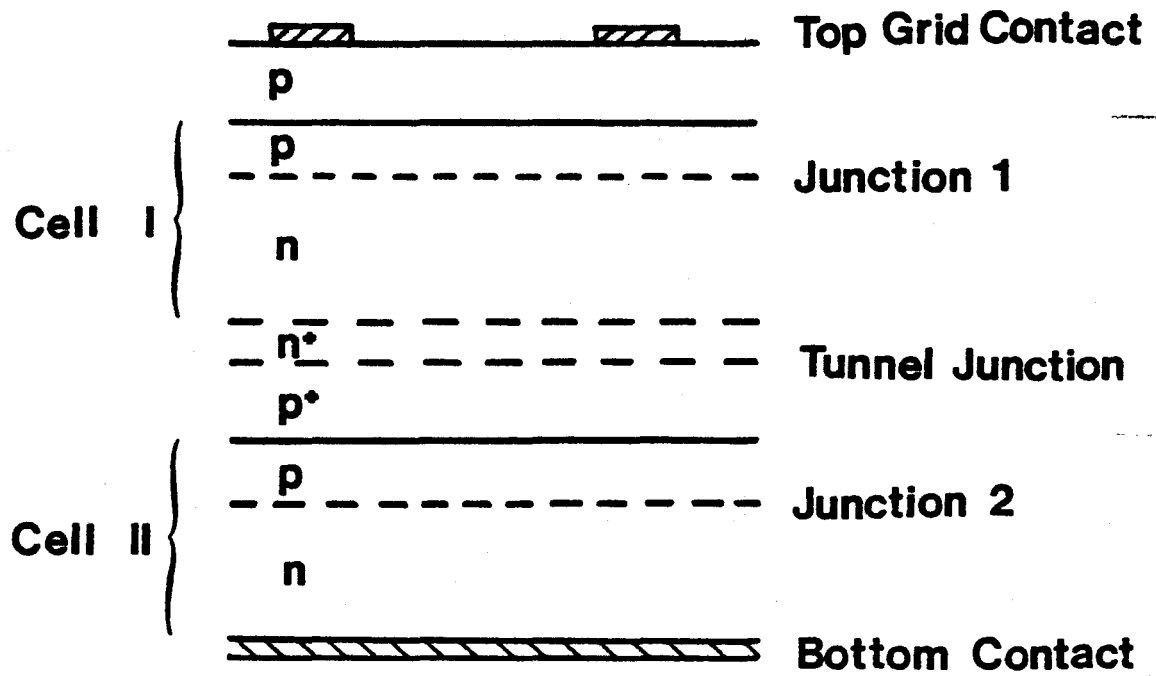


Figure 5. Drawing of an MBE-fabricated multilayer integrated structure.

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