

letters

with a missile defense in place on both sides the path will be cleared to parallel and simultaneous reductions by the US and USSR in the numbers of their offensive weapons. This is the position of our government's negotiators in Geneva, and it seems to me to be realistic. If each side has a defense that is 90% effective, meaning only one in ten warheads can reach its target, it will certainly seem less attractive to the defense planner to continue putting defense dollars or rubles into these very expensive weapons, and he may well look to other ways of spending his money. After all, if it became known that 90% of our B1-B bombers and their payloads would be shot down on approaching Soviet air space, Senator Sam Nunn would not be likely to get up on the floor of the Senate to say, "Let's build ten times as many B1-Bs to overwhelm this defense." He would be more likely to say, "Let's scrap this ineffective weapons system and find a better way of spending our defense dollars."

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12/85

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Noncrystalline semiconductors

The recent letter of William Paul and Henry Ehrenreich (August, page 13) is an ironic example of how an attempt to provide "a historical perspective" about an important field can itself "perpetuate and even extend some prevalent misconceptions." Rather than clarifying the single sentence by Hellmut Fritzsche in his review (October 1984, page 34), the long narrative of Paul and Ehrenreich, while attempting to be factual, actually serves to distort the situation in a major way.

Amorphous silicon alloys are important because they are able to mimic the semiconducting properties of crystalline silicon, while possessing the additional quality that they can be prepared rapidly over large areas in a thin-film geometry. Beyond the economic benefits, however, the possibility of

controlled alloying of the amorphous materials promises greater flexibility and consequently improved device performance using heterojunction configurations. As just one example, multiple-junction amorphous solar cells are now outperforming¹ single-junction cells. This accomplishment required several steps:

- ▶ a sharp reduction in the defect approximation so that the density of states near the Fermi energy is less than approximately $10^{16} \text{ cm}^{-3} \text{ eV}^{-1}$
- ▶ the ability to modulate the energy gap by alloying while retaining low defect concentrations
- ▶ the development of materials that do not degrade under device operating conditions.

If any of these problems were to remain unsolved, interest in amorphous silicon alloys would soon go the way of that in pure amorphous silicon, which was investigated extensively in the early seventies but has not been discussed recently because the defect concentration could not be lowered to electronically acceptable levels.

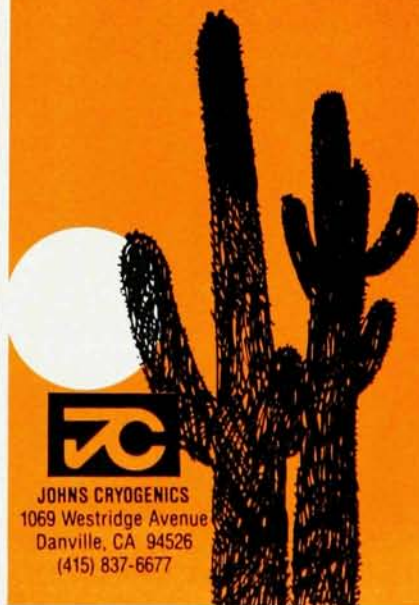
Interest in the field of tetrahedral amorphous semiconductors was sustained by the accidental discovery of hydrogenated amorphous silicon, as detailed by Paul and Ehrenreich, which was a major step towards achieving the first of the previously mentioned goals. However, some residual defects always remain in this material, and it degrades when exposed to sunlight² to the point where its use in devices becomes questionable. Furthermore, attempts³ to make high-quality hydrogenated amorphous silicon-germanium alloys for band-gap modulation failed. Obviously, a new concept was essential.

It is now clear that the deliberate development of fluorinated amorphous materials⁴ led to the simultaneous accomplishment of all three goals. The chemical explanation of the problem of the origin of the density of states in the silicon-germanium alloys and of fluorine's role in solving this crucial problem was given^{1,5,6} in several papers. Subhendu Guha (Energy Conversion Devices), in an invited paper at the most recent International Conference on Amorphous and Liquid Semiconductors, just held in Rome (2-6 September 1985), not only documented⁷ the stability of devices based on these materials but also reported experimental results showing the low density of defect states so necessary to making these materials useful. He described as well the development of semiconductor-grade alloys of different band gaps. That fluorine plays the suggested role has been independently confirmed by a host of investigators, as is evident from the papers presented at the same international conference. At least 14 papers at this

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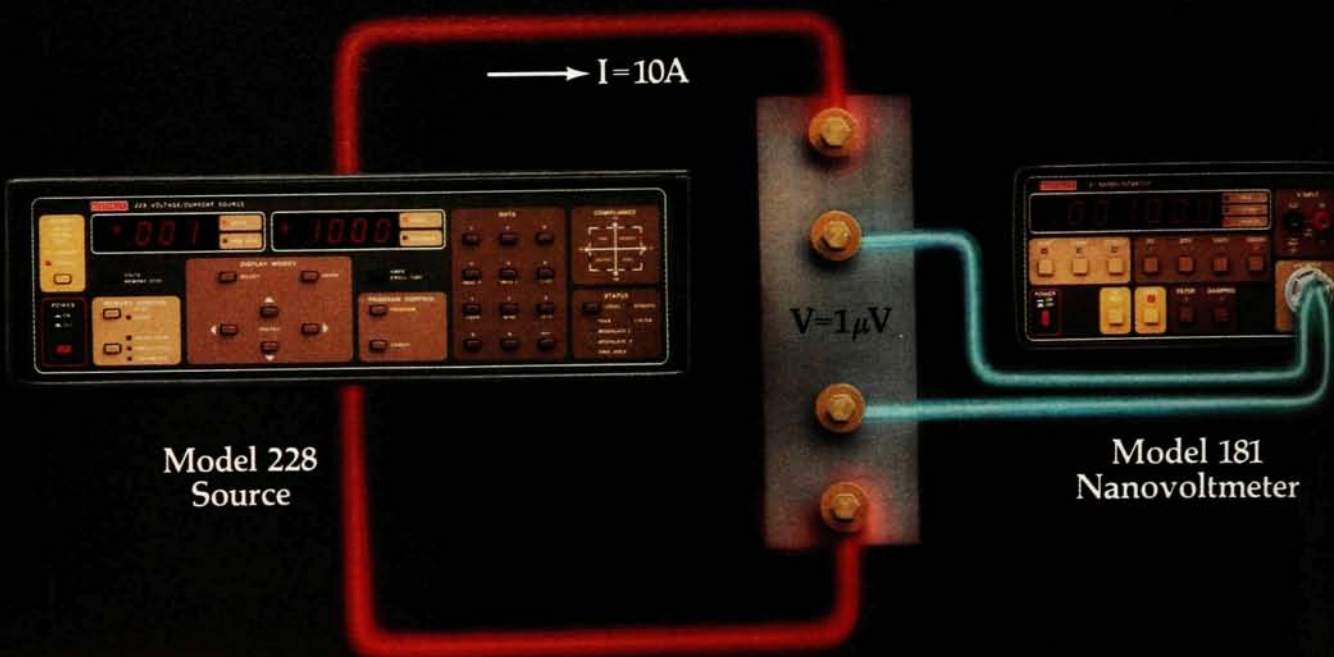


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conference reported on fluorinated materials, an eloquent testimony to the interest in such alloys. Hiroyoshi Matsumura and his collaborators (Hiroshima University) corroborated⁸ the improvements in both stability and defect density of amorphous-silicon-based materials that are directly attributable to the introduction of fluorine, while Shunri Oda and his group (Tokyo Institute of Technology) and Shinya Tsuda's group at Sanyo Electric Co both confirmed^{9,10} our previously reported result that fluorine sharply improves the quality of amorphous silicon-germanium alloys to levels acceptable for use in devices.

Paul and Ehrenreich state, "Thus far, the effect of the addition of fluorine to the glow-discharge plasma has been insufficiently documented in the literature for a final conclusion regarding its efficacy." They also imply that even A. Madan has some doubts in this regard. We find it interesting that both Madan and Paul coauthored papers at the Rome conference on just this subject. A. H. Mahan, B. von Roedern and Madan found¹¹ that incorporation of fluorine in amorphous silicon-carbon alloys decreased the density of defect states and increased the photoconductivity. A recent paper by Paul's group showed¹² that fluorine provided "an order-of-magnitude improvement in the photoconductivity" of amorphous silicon-germanium alloys and presented as their major conclusion, "The effect of fluorine is beneficial." We defer to this objective source for the final word.

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THE AUTHORS REPLY: The opening broadside notwithstanding, the letter by S. R. Ovshinsky and D. Adler does not address the historical perspective concerning the development of the amorphous-semiconductor field that we discussed in our letter.

We wish only to comment on the objections to our conservative opinion that any beneficial effects fluorine may have are not yet well understood. The Ovshinsky-Adler discussion confuses the facts of the matter by failing to distinguish between the effects of incorporation of about one atomic percent of fluorine in the film and the effects of fluorine in the plasma.¹ The real cause of the observed improvements in photoconductivity and device stability remains to be established by experiment.

We are entirely in agreement with Ovshinsky and Adler that amorphous semiconductors have become increasingly important and that the contributions of Ovshinsky and his associates (including Adler and Hellmut Fritzsche) have had an important catalytic effect on their development. The latter point was already stressed² in an early National Materials Advisory Board study chaired by one of us.

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11/85

Proton storage ring

Your "Search and discovery" story (June, page 21) reported the news of the first operation of the new Proton Stor-

continued on page 114



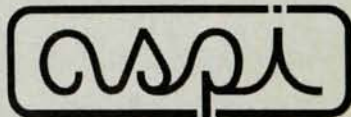
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