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IONIZED CLUSTER BEAM DEPOSITION**Allen R. Kirkpatrick****Eaton Ion Materials Systems
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Ionized Cluster Beam (ICB) deposition, a new technique originated by Takagi of Kyoto University in Japan, offers a number of unique capabilities for thin film metallization as well as for deposition of active semiconductor materials. ICB allows average energy per deposited atom to be controlled and involves impact kinetics which result in high diffusion energies of adatoms on the growth surface. To a greater degree than in other techniques ICB involves quantitative process parameters which can be utilized to strongly control the characteristics of films being deposited. ICB is easily amendable to process automation and offers opportunity to utilize film character-process parameter closed-loop control routines.

In the ICB deposition process, material to be deposited is vaporized into a vacuum chamber from a confinement crucible at high temperature. Crucible nozzle configuration and operating temperature are such that emerging vapor undergoes supercondensation following adiabatic expansion through the nozzle. Atomic aggregate clusters, each consisting of roughly 10^3 atoms, are formed. The clusters can be ionized by impact ionization and then accelerated toward the substrate by a high potential. It is possible to control average energy per atom from a fraction of an electron volt to more than 100eV. Upon impact, the clusters break up in a manner which converts substantial kinetic energy into surface diffusion energy. A number of advantageous phenomena result.

ICB is being utilized for laboratory deposition of semiconductor device metallization, for dielectric films and for semiconductor materials. In general, very high quality films with remarkable characteristics are achieved. ICB is new technology for which applications development is only beginning and prospective applications to photovoltaic devices are yet to be well defined. One important area which can be specified and is already being addressed involves use of ICB for deposition of the active semiconductor materials for thin film cells. Utilization for metallization systems is another possibility which might be of near term importance.

It should be recognized that ICB is a modified vacuum evaporation process for which economic considerations will be similar to those associated with standard evaporation. Consequently it is reasonable to assume that films to be deposited

by ICB should be a few microns or less in thickness and probably then must be limited to providing metallization base layers and fine grid patterns. Beyond this constraint ICB offers technical characteristics and process controls which might be very effectively adapted to the needs of advanced photovoltaic metallization systems.

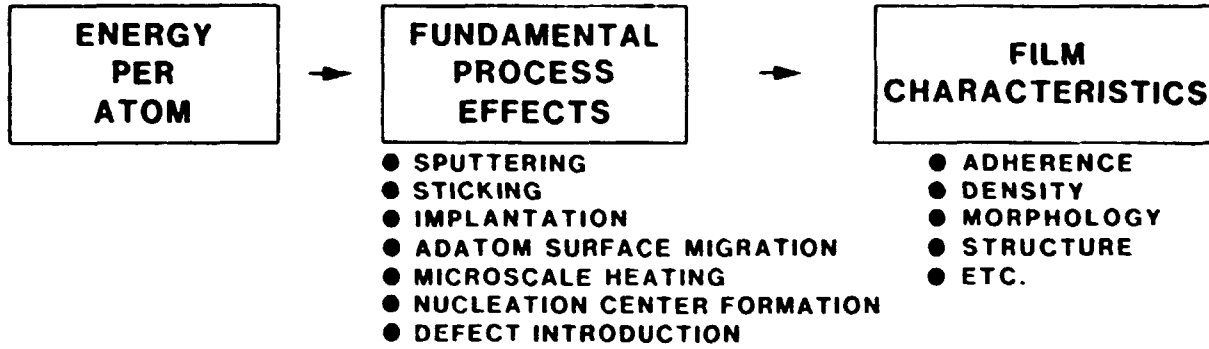
The most important features of ICB relative to deposition of metal films include:

- o Ability to achieve higher quality films onto lower temperature substrates
- o Better process control over film characteristics
- o Spatial directionality of deposition
- o Ease of scale up to very high throughput

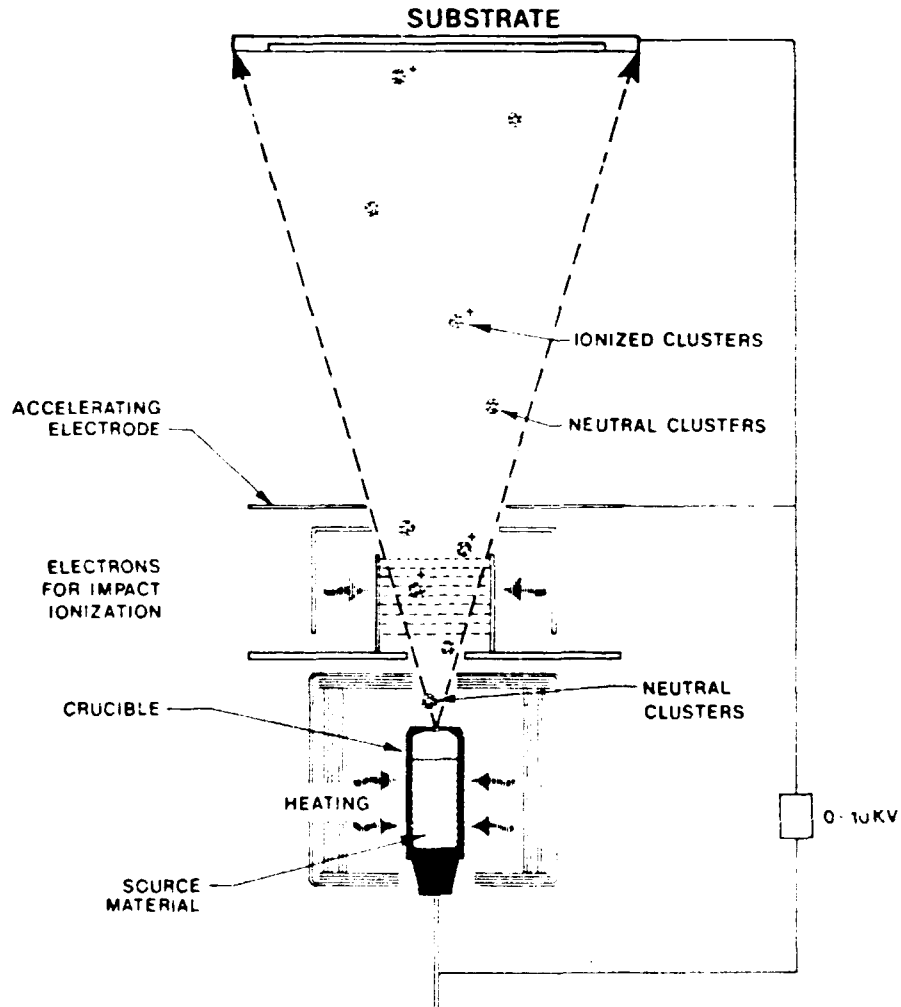
Applications of ICB to solve photovoltaic metallization system problems might involve:

- o Better technical characteristics (structure, adherence, density, morphology, etc.)
- o Lower temperature demands
- o Elimination of interface intrusions with low cost materials
- o Superior long term stability characteristics
- o Compatibility with sequential total device fabrication involving thin film semiconductors and transparent conductive coatings
- o Better compatibility with pattern definition processes
- o Improved material use efficiency
- o Ease of scale up to very high throughputs and total automation

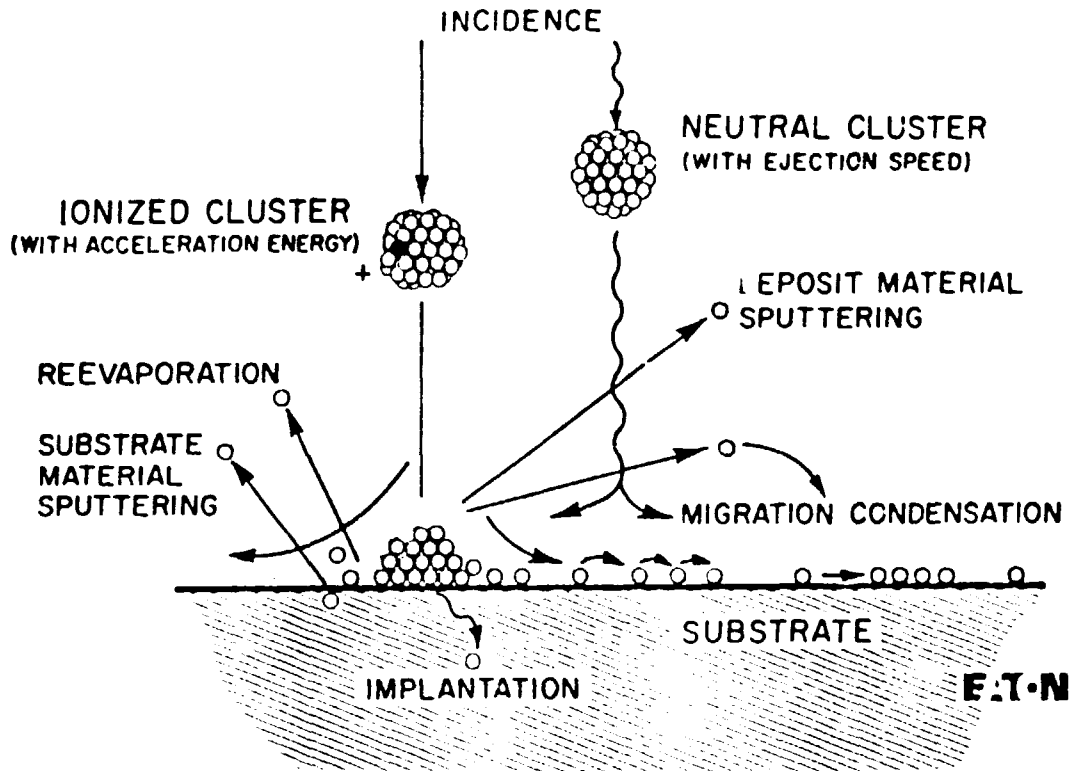
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Basic ICB Deposition Configuration



Cluster Impact Phenomena

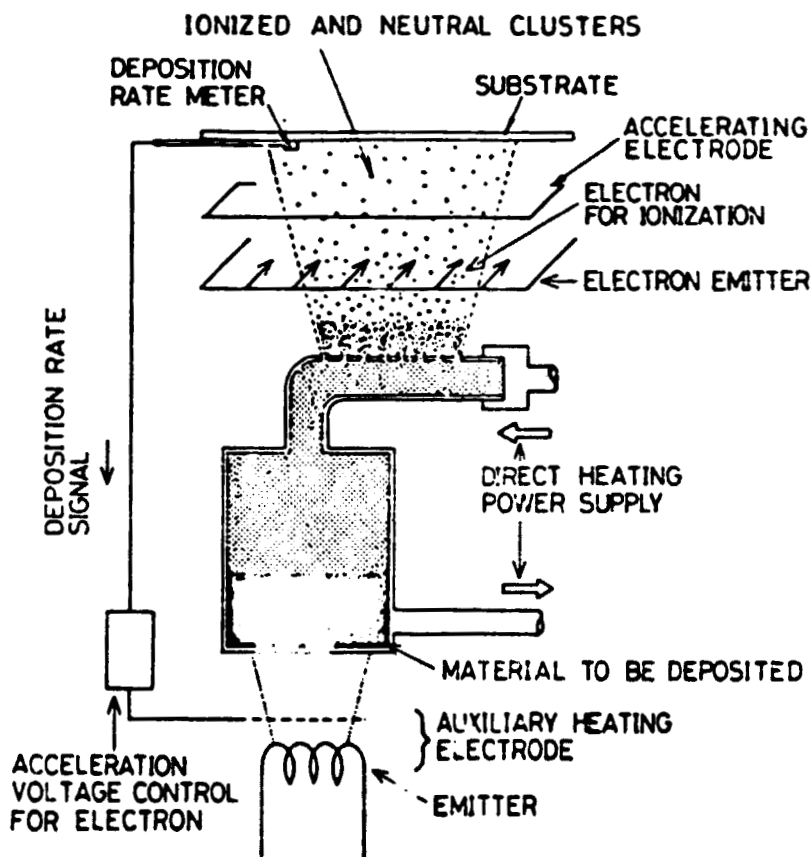


Major Features of ICB

- **ABILITY TO ADJUST AVERAGE ENERGY PER DEPOSITION ATOM OVER 0.01-100⁺ eV RANGE**
- **EFFECTIVE CONVERSION OF CLUSTER KINETIC ENERGY TO ADATOM SURFACE ENERGY DUE TO SNOWBALL EFFECT**
- **INHERENT CLEANSING ACTION BY SPUTTERING AND MICRO-SCALE HEATING**
- **ENHANCED REACTIVE PROCESSES DUE TO IONIC CHARGE PRESENCE**

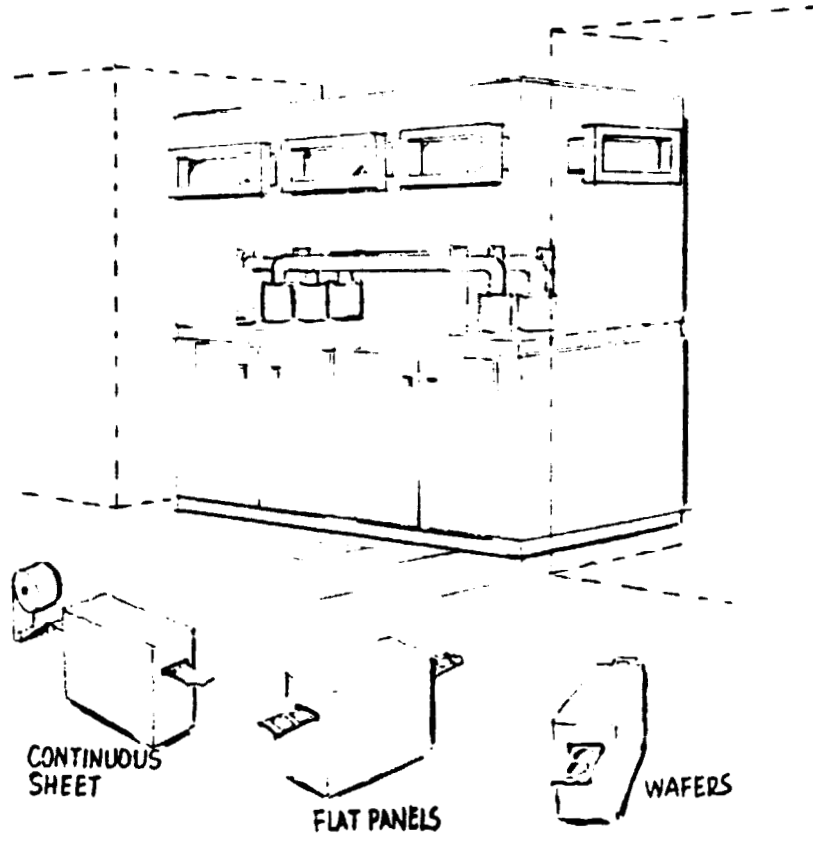
Materials by ICB to Date

| | | | |
|--------------|----------------|------------|--------------------------|
| Cu | Si | BeO | Organic Materials |
| Ag | α -Si:H | GaN | |
| Au | ζ -FeSi | ZnO | |
| Pb | GaAs | SiC | |
| Al | CdTe | | |
| Au-Sb | ZnS | | |
| | InSb | | |
| | GaP | | |
| | PbTe | | |
| | ZnSb | | |
| | MnBi | | |



ICB Production

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Technical Prospects of ICB for Thin Films

- **BULK MATERIAL PROPERTIES**
 - **CONTROL OF MORPHOLOGY**
 - **SELECTION OF GROWTH STRUCTURE**
 - **HIGH T EQUIVALENT PROCESSES AT LOW T**
 - **PROCESS CLEANLINESS**
 - **EFFICIENT REACTIVE FORMATION**
 - **CONVENIENT DOPING**
 - **QUANTITATIVE PARAMETERS**
 - **AUTOMATION**
 - **CLOSED-LOOP CONTROL**
 - **MATERIAL USE EFFICIENCY**
-
- **SCALE UP CAPABILITY**
 - **VERSATILITY**

Prospective Advantages of ICB for PV Metallization Systems

- **BETTER TECHNICAL CHARACTERISTICS (STRUCTURE, ADHERENCE, DENSITY, MORPHOLOGY, ETC.)**
- **LOWER TEMPERATURES**
- **ELIMINATION OF INTERFACE INTRUSION EFFECTS WITH INEXPENSIVE METALS**
- **SUPERIOR LONG TERM STABILITY CHARACTERISTICS**
- **TOTAL DEVICE FABRICATION COMPATIBILITY**
- **BETTER COMPATIBILITY WITH PATTERN DEFINITION PROCESSES**
- **IMPROVED MATERIAL USE**
- **EASE OF SCALE UP TO VERY HIGH THROUGHPUTS AND TOTAL AUTOMATION**

DISCUSSION

SCHRODER: If you deposit a compound nonreactively I assume you need one crucible per material.

KIRKPATRICK: It depends upon the material. If you have a material like cadmium telluride where the vapor pressures of the two constituents are similar then you can put cadmium telluride into the crucible; but if you want to deposit something like gallium arsenide you need a gallium crucible and an arsenic crucible.

CAMPBELL: Have you ever done any of the refractory metals, like titanium or sodium?

KIRKPATRICK: No. Everyone asks; you have to be able to get reasonable vapor pressure of those metals. Now, I think maybe titanium you can do, but a lot of people ask about tungsten and molybdenum; we make the ion sources out of those metals. It's not out of the question, it depends upon work that has never been done utilizing organometallics, and I think some work will be done on that, but I don't know the answer yet.

BACHNER: What's a piece of equipment like that cost?

KIRKPATRICK: About a half million dollars.

HOGAN: With something like silicon, how do you do the doping?

KIRKPATRICK: You bring in phosphine or diborane as background gas.

HOGAN: What happens if you go to a higher than a 50% cluster ion position?

KIRKPATRICK: Nothing, I think you just end up breaking up some of the cluster and you just don't gain anything, it's just not necessary.

HOGAN: Would it be possible then to directly add a direction to those clusters, to the substrate?

KIRKPATRICK: Yes, because experiments have been done on that, but I think it would be impractical to try and do it now, for real films. I see that as maybe occurring in maybe 10 years or so that you could do directional beaming. It's kind of like ion implantation; when ion implantation first came out 20 years ago, everybody said "Gee, this is the way to do doping, just where we want it." The first machines for that are just hitting the market now. It has taken 20 years for the machine technology to come along and I think the same will be true with ICB.

SCHWUTKE: I would like to congratulate you, if all these things work the way that you explain them, it's a wonderful machine, with a terrific list of all the good things it can do. Would you like to comment on what can go wrong?

KIRKPATRICK: I don't want to be too glib, I don't know what can go wrong. We built machines, more or less, to the instructions of the people in Japan who invented the process and the first several machines that we've

built, the customers were waiting there for them the moment they were finished and they checked them out and took them away and we didn't get any operating experience ourselves. One week ago our own machine became operational, and we now have a laboratory where we are doing our own work. Very soon we will have two machines in there, and people will be invited to come and see this process.

SCHWUTTKE: What is the reliability of the ion sources, how long can the source operate what kind of power do you use, and what kind of crucible material are you using? Would you like to comment on that?

KIRKPATRICK: Sure, can I start with crucible material? Our standard crucible now is POCO graphite, semiconductor-grade graphite cleaned up after machining by high temperature, storage in chlorine gas; for most deposition materials that crucible lasts a long time, and --

SCHWUTTKE: What's a long time? A year, a day, an hour?

KIRKPATRICK: I don't know, nobody's run one long enough to wear it out. If you are doing a metal that doesn't wet the graphite you just keep putting in new charge; if you deposit silicon from that crucible you form silicon carbide on the crucible surfaces and the crucible becomes embrittled and after refilling the crucible about three times, you are better off to throw it away because eventually it will crack. The ion sources are difficult to build. Our first ones have deteriorated after running for a few months, and we have to replace many of the components, but I think there's just engineering experience needed there.

SCHWUTTKE: What are the dimensions of the ion source?

KIRKPATRICK: About the size of a tomato-juice can.

SCHWUTTKE: So you can actually load this thing up, or what? Do you put silicon in it? You can put in a kilo of silicon?

KIRKPATRICK: No, the crucible is smaller. You could build larger crucibles; our crucibles have 10 cc charge capacities, so you can put in 10 cc of silicon.

SCHWUTTKE: And then, theoretically, you could run this machine continuously for how long? Deposition, I mean.

KIRKPATRICK: I don't know. Until the crucible runs out.

SCHWUTTKE: There are there other problems when things are in operation for some time. I try to find out if it can run two minutes or 2 hours continuously.

KIRKPATRICK: Oh, you can run it two hours continuously, they probably have been run a week continuously and then needed maintenance but I think production machines will run like production ion implanters.

SCHWUTTKE: But you have no real data from Japan.

KIRKPATRICK: Not yet.

SCHWUTTKE: We just assume that the machine will do certain things.

KIRKPATRICK: Oh, no. The Japanese complain very loudly when a machine doesn't work.

COMMENT: What about when it does work? They don't complain.

COMMENT: How long have you been in the field?

KIRKPATRICK: We delivered the first of these machines last summer, so total experience on this equipment is what, maybe eight or nine months.

R. VEST: You mentioned that they have done an epitaxial gallium arsenide on gallium arsenide. Now this is also being done by MBE; what's the advantage of your approach?

KIRKPATRICK: There is a lot less experience on ICB than there is on MBE. I can't tell you about relative material quality, but if ICB can achieve the same material quality as MBE, then ICB has practical advantage totally over MBE. This is a normal high vacuum process, and you can scale it to anything you want to talk about; MBE isn't that way and for high-throughput production equipment, one of the things I should have mentioned, this (ICB) is going to be like sophisticated evaporation or sputtering equipment. It uses the same kind of vacuum components, the same sort of chamber, the same kind of mechanical handling. It needs more power supply, so there will be an incremental additional cost, but it is not anything like a factor of 2.

DUTTA: How do you handle patterns? Do you use shadow masks?

KIRKPATRICK: So far we have not patterned anything except by accident by putting things into the cluster stream. You can certainly do patterning by shadow masks, and the patterns are extremely sharp, even when the mask is a long way away from the substrate. I think you can also do very good patterning with this technique using photoresist and liftoff, because you can deposit the film at low substrate temperature and it will adhere, and it will be easy to do a nice clean liftoff afterward.

AMICK: Allen, would you say what the power consumption used or pulled for a small, 2-wm or larger, source?

KIRKPATRICK: On the small one, when you are running silicon and you are running a few hundred Angstroms a minute, the ion source is drawing about 1500 to 2000 wa ts. On a curtain source I don't know; I know that you would need approximately 3 kW to keep a 2-foot-long tube hot, and I'm not sure how much goes to heating the reservoir.

AMICK: What about vacuum pumps and the use of associated equipment? What's the total input power?

KIRKPATRICK: I'm sorry, I was counting power supplied to the source. It certainly needs the same kind of vacuum support equipment you have with an evaporator. It is very comparable to electron beam evaporation in total power consumption.

SCHWUTTKE: May I ask the last question, without being facetious, did you get any feedback on the films deposited in Japan on the structure? I mean, do they send you samples or anything of that nature?

KIRKPATRICK: They don't send the samples. I think they are pretty good. The first customer is buying a second machine.

SCHWUTTKE: This is too good to be true. If you are right, and you really can do, and have the control they claim you can achieve, and you go basically from amorphous to single-crystal -- I haven't seen any samples yet. I wonder if you've got some?

KIRKPATRICK: Well, in two or three months, you are perfectly welcome to come and get some samples from us.

SCHWUTTKE: I'll have the same problem that I had with Ovshinsky. He has been promising me samples for a year.

LANDEL: Can you add anything about the uniformity of deposition across the deposition area? Particularly, say, with and without the ionization; with the ionization is the way you like to run it.

KIRKPATRICK: The machine that I showed you a photo of is a single-substrate-at-a-time machine. It brings things in on a walking-beam transport system, and the deposition area is a 7 in. diameter circle, and we guarantee that the process that you can measure -- thickness, whatever -- will be uniform to within $\pm 5\%$ over a 10-cm square.

MRIG: Do you have any idea of the efficiency of the amorphous silicon being deposited by the Japanese company?

KIRKPATRICK: No, and I don't think we are going to find out.

MRIG: Can this be made into continuous process somehow, or is it going to be a batch process?

KIRKPATRICK: This is very easily a continuous process.

HOGAN: Getting back to definition, did you say there had not been anything done with photoresist, that you know of?

KIRKPATRICK: Nothing published.

HOGAN: My only concern would be the higher energy and possible polymerization of photoresist caused by microheating.

KIRKPATRICK: You do get microheating, but coming from an ion implanter company, I do know the answer to that. Everyone uses photoresist as an ion implant mask. You are implanting at 60 to 200 Kev, you polymerize the surface of the photoresist but it still comes off.

ZWERDLING: Can you provide a background temperature heating of the substrate deposition surface, if you need it, or is it advisable?

KIRKPATRICK: Yes.

ZWERDLING: Can you deposit amorphous metals other than amorphous silicon?

KIRKPATRICK: I believe you can deposit amorphous metals just as easily as you can amorphous silicon.

ZWERDLING: And with regard to metallization would you be able to deposit diffusion barrier material followed by the metal for the metallization of it?

KIRKPATRICK: I wasn't here yesterday, so what are diffusion barrier materials right now?

ZWERDLING: Well, there is a variety of them.

COMME 1: Titanium, as an example.

KIRKPATRICK: I think so, but I don't know.

ZWERDLING: If you could deposit that as well as metal without breaking the process.

KIRKPATRICK: Yes, in the equipment that we presently sell you have a carousel with many crucibles available to you. You can deposit multiple-layer films without breaking vacuum. You only have one ion source, but you can inject different crucibles with different materials.