LASER ASSISTED DEPOSITION

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INTRODUCTION

Metallization of semiconductor devices is conventionally accomplished by a multistep process involving photolithographic pattern definition, metal film deposition, and liftoff or etching. Laser-assisted pyrolysis and photolysis techniques have recently emerged as novel, maskless, one-step processes for well-resolved, localized metal film growth on semiconductor substrates. Infrared, visible, or ultraviolet lasers have been used to deposit metal films on selected substrates, either thermally, as in laser chemical vapor deposition (LCVD), or non-thermally by photodissociation or organometallic vapors.

Laser-Assisted Thermal Deposition

Chemical vapor deposition (CVD) of metals is conventionally performed by resistively or inductively heating an appropriate substrate in a reactive atmosphere, with pyrolysis reactions at the substrate surface providing the basis for film growth. Pulsed or CW lasers of suitable wavelengths may be used to selectively heat localized areas of substrates which absorb at these wavelengths. The use of a laser as a heat source for chemical vapor deposition (LCVD),(1) particularly for photovoltaic metallization systems applications, offers several distinct advantages: (1) the spatial resolution and control required for maskless production of fine line metal grid structures; (2) localization of the heating to a shallow, surface layer, resulting in limited distortion of the substrate; (3) the possibility of cleaner films due to the small volume heated; and (4) the ability to interface easily with laser annealing(2) and laser diffusion(3) of solar cells.

Allen and Bass(4) have used a CO_2 laser to deposit nickel on quartz substrates from gaseous $Ni(CO)_4$. LCVD metal film thicknesses tend to be self-limiting, with a maximum thickness of 550 Å being obtained for nickel. Electroplating or electroless plating techniques may have to be employed in order to build up the requisite film thickness for solar cell applications.

Visible or ultraviolet lasers may also be used to selectively heat the substrates. Excimer lasers, which operate at ultraviolet wavelengths, may be more effective than long-wavelength lasers for LCVD applications, as silicon has a direct bandgap transition at ultraviolet wavelengths. As a result, the ultraviolet radiation is absorbed much more strongly at the silicon surface and does not penetrate as deeply into the substrate, resulting in precisely localized heating. Other advantages of excimer lasers include: (1) greater electrical efficiency resulting in lower fabrication costs; (2) low coherence, alleviating interference problems such as speckle; and

(3) a typically high transverse mode structure, producing a beam of uniform intensity over a large area.

Photodissociative Metal Deposition

One of the most exciting new techniques for metal film deposition that has recently emerged is laser-induced photodecomposition of gas-phase organometallic compounds. The fundamental difference between this technique and laser chemical vapor deposition is that, instead of relying on localized substrate heating and subsequent pyrolysis reactions at the substrate surface to achieve film deposition, the photons non-thermally sever bonds in gas-phase organometallic molecules, liberating metal atoms which condense on the laser-illuminated regions of the substrate, forming a film. This technique is capable of very high resolution patterned film deposition for two reasons. Firstly, the deposited metal linewidths are independent of the substrate absorption or thermal conductivity, resulting in finer resolution and greater uniformity over the entire substrate due to the insensitivity to local variations of thermal conditions. Secondly, the ultraviolet lasers that are generally used in this technique have considerably smaller diffraction-limited spot sizes than visible, or infrared lasers, resulting in deposited linewidths as small as 0.7 micron.(5)

Ehrlich, Deutsch and Osgood(5)-(8) have performed a variety of experiments on photodissociative metal deposition using both pulsed (excimer lasers, 1-100 mJ, 10 ns) and CW (frequency-doubled Ar^+ laser, 10 μW - 3 mW) UV lasers. In one of their most interesting experiments,(6) a two-step process was used to deposit Cd, Al, and Zn patterned films from metal-alkyl vapors. In the first step, called prenucleation, a focused UV laser was used to irradiate the substrate in the requisite pattern, photodissociating a thin, adsorbed layer of metal-alkyl molecules. The laser was then defocused to illuminate the entire substrate, causing film growth to occur selectively in the prenucleated regions. These experiments also indicated that films of one metal, e.g., Al, may be grown on nucleation centers of a second dissimilar metal, e.g., Zn. This is of particular interest for solar cell applications, whre a two- or three-metal system often has to be employed for diffusion barrier and galvanic buffering purposes.

Draper(9) has deposited both Cr and Mo using off-resonance laser-induced dielectric breakdown of metal carbonyl vapors with a pulsed CO_2 laser. Solanki et al.(10) used a pulsed copper hollow cathode laser at 260 nm, utilizing the multiphoton absorption that occurs at this ultraviolet wavelength for carbonyl molecules, to deposit Cr, Mo, and W films. The laser was operated at 150 mW peak power with pulse widths of 120 μs. In another set of experiments, Coombe and Wodarczyk(11) used KrF (249 nm) and XeCl (308 nm) excimer lasers to induce the localized deposition of Zn and Mg films from the pure metal vapors. The laser pulses used in these experiments were typically 20 ns in duration and carried energies of up to 20 mJ (KrF) or 5 mJ (XeCl).

Conclusions

Applications of laser-based processing techniques to solar cell metallization will be discussed. Laser-assisted thermal or photolytic maskless deposition from organometallic vapors or solutions may provide a viable alternative to photovoltaic metallization systems currently in use. High power, defocused excimer lasers may be used in conjunction with masks as an alternative to direct laser writing to provide higher throughput. Repeated pulsing with excimer lasers may eliminate the need for secondary plating techniques for metal film buildup. A comparison between the thermal and photochemical deposition processes will be made.

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Potential Advantages of Laser Deposition Techniques for Photovoltaic Systems

- **High Resolution**
- **Maskless Process**
- **Clean And Contamination - Free**
- **In-Situ Sintering**
- **Low Contact Resistance**
- **Low Cost**

A Conventional Metallization System Employs a Sequential Multistep Process:

Photolithographic Pattern Definition

Film Deposition

Lift-Off Or Etching

Laser-Assisted Metallization Techniques Are Essentially One-Step Processes:

Laser-Surface Interaction
Resulting In
Localized Film Growth

Photovoltaic Metallization System

Screen Printing
- Electroplating Not Required
- Poor Resolution
- Limited To One Metal — Ag
- Possibility Of Low Shunt Resistance, Low Lifetimes
- High Contact Resistance

Photolithographic Definition
- Better Resolution
- Variety Of Metals (Diffusion Barrier)
- Electroplating Required
- Multistep Process

Laser-Assisted Deposition
- Submicron Resolution
- Variety Of Metals
- Electroplating May Not Be Required
- One-Step, Maskless Process

Laser-Assisted Deposition Techniques

Pyrolytic Deposition (Thermal)

- Laser Chemical Vapor Deposition (LCVD)
- Laser Deposition From Solutions

Photolytic Deposition (Non-Thermal)

- Laser Photodissociation Of Vapors
- Laser Photodissociation Of Solutions

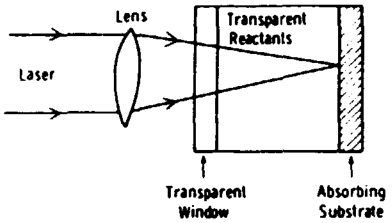
Pyrolytic Deposition

Laser Chemical Vapor Deposition (LCVD)

C. P. Christiansen and K. M. Lakin (1977)
Electrical Engineering Department
University of Southern California

S. D. Allen and M. Bass (1979)
Center for Laser Studies
University of Southern California

W. Roth, H. Schumacher, and H. Beneking (1983)
Institute of Semiconductor Electronics
W. Germany



Schematic of LCVD Apparatus

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Dwg. 7779A96

Advantages

- Spatial Resolution And Control — Maskless Process
- Limited Distortion Of Substrate
- Possibility Of Cleaner Films
- Convenient Interfacing With Laser Annealing And Laser Diffusion Of Solar Cells

Disadvantages

- LCVD Metal Film Thickness Self-Limiting — Require Electroplating
- Direct Laser Writing Relatively Slow Process

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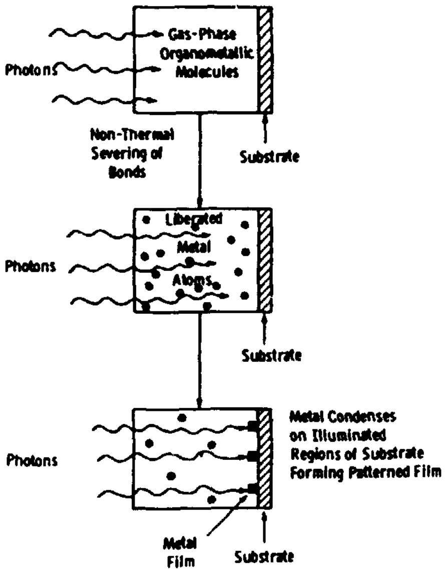
Photolytic Deposition

Laser-Induced Photodecomposition of Gas-Phase Organometallic Compounds:

This Technique Is Fundamentally Different from Thermally Based Laser Processes



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Laser-Induced Photodissociation Experiments Performed by:

D.J. Ehrlich, T.F. Deutsch, And R.M. Osgood
(1979-1982)
M.I.T. Lincoln Laboratory

Lasers

- **Pulsed Excimer Lasers**
  λ = 157-350 nm
  Energy = 1-100 mJ
  Pulse Width = 10 ns,
  Repetition Rate = 1-150 Hz
- **CW Frequency-Doubled Ar^+ Laser**
  λ = 257.2 nm
  Power = 10 μw - 3 mW

Encapsulant Gases

$Cd(CH_3)_2$
$Zn(CH_3)_2$
$Sn(CH_3)_4$
$Ga(CH_3)_3$
$Bi(CH_3)_3$
$Si(CH_3)_4$
$Ge(CH_3)_4$
$Al_2(CH_3)_6$

$Fe(CO)_5$
$W(CO)_6$
$Cr(CO)_6$

CF_3I
$SnCl_4$

Two-Step Deposition Process

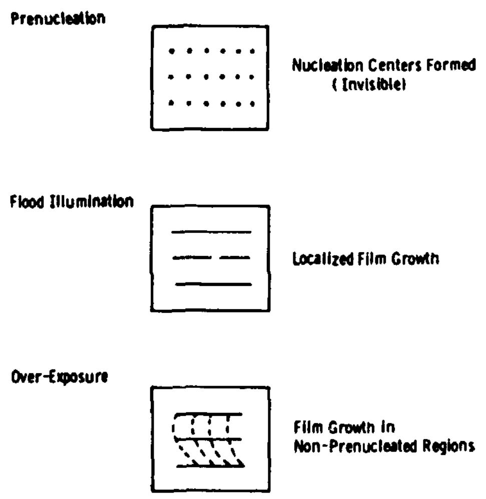
Prenucleation:

1. Substrate Exposed To High Pressure (~ 20 Torr) Of Zn $(CH_3)_2$
2. Chamber Evacuated To << 1Torr
3. Focused CW Laser Beam (λ = 257.2 nm) Scanned Across Substrate In Requisite Pattern Forming Zn Nucleation Centers

Film Growth:

1. Chamber Filled To 10 Torr Of Zn $(CH_3)_2$
2. Substrate Flood Illuminated Using Defocused Laser Beam
3. Film Growth Occurs Selectively In Prenucleated Regions

Films Of One Metal, e.g. Al, May Be Grown On Nucleation Centers Of Another Metal, e.g. Zn



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Other Laser-Induced Photodeposition Experiments

R. Solanki, P.K. Boyer, J.E. Mahan,
And G.J. Collins (1981)

Colorado State University

Pulsed Copper Hollow Cathode Laser

λ = 269 nm
Power = 150 mW
Pulse Width = 120 μs

Cr, Mo, And W Films Deposited From
Metal-Carbonyl Vapors

R.D. Coombe And F.J. Wodarczyk (1980)

Rockwell International

Pulsed KrF Excimer Laser

λ = 249 nm
Energy = 20 mJ
Pulse Width = 20 ns

Pulsed XeCl Excimer Laser

λ = 308 nm
Energy = 5 mJ
Pulse Width= 20 ns

Zn And Mg Films Deposited From
Pure Metal Vapors

C.W. Draper (1980)

Western Electric Research Center

Pulsed CO_2 Tea Laser

λ = 10.6 μm
Energy = 4-5 J
Pulse Width = 170 ns

Cr And Mo Films Deposited From
Metal-Carbonyl Vapors

Advantages

- **Possibility Of Depositing Two Or More Dissimilar Metal Films Over Each Other**
- **Higher Resolution Obtainable Than With Thermal Techniques**
- **Defocused, High Power, Pulsed Excimer Laser May Be Used With Mask For Faster Deposition**
- **Repeated Pulses For Film Buildup**

Advantages of Excimer Lasers

- **Direct Bandgap Transition → Strongly Localized Heating At Silicon Surface (For Thermal Deposition Techniques)**
- **Greater Electrical Efficiency → Lower Costs**
- **Low Coherence → Absence Of Speckle**
- **High Transverse Mode Structure → Uniform Intensity Over Large Area**

Applications To Photovoltaic Metallization Systems

Laser Thermal Deposition From Vapors (Or Solutions):

- **Clean, Maskless Process**
- **Possibility Of Interfacing With Laser Annealing And Diffusion Techniques**
- **Ability To Electroplate On Thin, Laser-Deposited Film For Rapid Metal Buildup**

Laser Photodeposition From Vapors (Or Solutions):

- **Possibility Of Two Or Three Layer Metal Deposition (Diffusion Barrier, Galvanic Buffering)**
- **Flood Illumination Using Mask For Rapid Throughput**
- **Possibility Of Using Repeated Laser Pulses For Film Buildup**

DISCUSSION

LANDEL: I'm sure there will be a number of questions. Let me exercise the chairman's prerogative to ask a few. You described the nature of the technique, but I'm sure the audience is hungering or thirsting for some information. For example, what has been put down? You talked about the ability to put down lines, in some cases you talked about films, which must be general films. It is not clear when you are talking about a line and when you are talking about a general surface area coverage. Finally, since you talked about thin films at the end of the last talk, you were talking about the problems that could be seen if you tried now to bond to the very thin films. Would you comment on any or all of those? Let me repeat them, let me take them in turn. The quantitative data: what has been put down in thin film or thin lines, since we are talking about metallization systems for cells?

DUTTA: Well, zinc, aluminum. The group at MIT have put down both films and lines, they have done several experiments on this technique and in the review paper they have written on the subject they have listed all of these encapsulant gases, so I assume they have put down all of these materials. They have talked in greater detail about aluminum, zinc and they have written lines, as well as deposited films; they have tried both. They have written lines using focused laser, and they've deposited films.

LANDEL: That wasn't clear. The second one was bonding to these lines. People have been talking about the difficulty of soldering to the various ink lines or lines put down in various ways. For example, the last speaker talked about the possibility of depositing the chemically metallo-organic systems, but those are so thin that she had to take special precautions to keep from simply dissolving them off again. Has anyone tried bonding to these sorts of lines?

DUTTA: You mean electroplating to these sort of lines? No, I have not seen it. There is a paper that this group (MIT) has written on using this metallization technique for MOS FETs, and they were able to measure device characteristics.

HYDE: What kind of deposition rate can you get with these techniques? What speed of layer buildup?

DUTTA: With this pyrolytic technique you are limited by your writing speed because you have to use speed that is compatible with the pyrolytic decomposition taking place at each spot. That makes it a relatively slow technique. I think you approach one micron or several microns a second. It is quite slow. With the photodissociated technique, the deposition rate is linear with the laser intensity and also with the density of organo-metallic gas.

LANDEL: You still have to prewrite, evidently, a nucleation site. Is that true?

DUTTA: That is true.

LANDEL: I think an appropriate question would then be, what sort of writing speed do you have there?

DUTTA: I think you could prewrite the pattern very rapidly -- 2000 cm per second.

SOMBERG: Would you care to comment on the cost of such a system, assuming it is done in a vacuum or some kind of chamber?

DUTTA: If you use an eximer laser -- that is a high-efficiency laser, so it is not as expensive as other laser systems -- I think the initial setting-up cost would be greater -- the initial optimization. All that would be greater than other techniques because it is a novel procedure, and I would assume that if things are properly optimized it would not be all that much more expensive to run.

SOMBERG: Are we talking in the order of, say, a quarter of a million dollars, a hundred thousand dollars? I am talking about the laser with the equipment, with the vacuum equipment.

DUTTA: The vacuum equipment should not be too expensive--a few thousand dollars. The laser would be the most expensive item.

SOMBERG: The other question I have, if I may, is: if you have to use a plating-up procedure on the pyrolytic technique, what is the advantage of the technique if you have to plate up?

DUTTA: You get very much better resolution than in the screen printing technique.

SOMBERG: I am talking about plating -- if you have to plate up, and if you were to use a photolithographic technique, what is the advantage of the pyrolytic technique if you have to plate up anyhow?

DUTTA: What is the advantage of the pyrolytic technique over the photolithographic technique?

SOMBERG: Yes.

DUTTA: You are still using maskless procedure -- the plating, of course, plates onto the metal. You don't have to use a mask during plating, so you are cutting down some of your process steps.

SOMBERG: Thank you.

AMICK: In describing the single-step photodecomposition gaseous organometallic technique, you say that after the metal atoms have been freed they will condense on a region of the substrate illuminated by the laser. Why are they so cooperative as to do that?

DUTTA: The laser is focused close to the substrate, so that the dissociation occurs right at the substrate and your dissociation is occurring in the absorbed layer at the surface of the substrate. It is dissociating only where the laser strikes it.

AMICK: If I go back from the substrate a little bit, unless it is a highly converging beam, I will also see dissociation there as well, so I would actually be depositing some metal atoms all over the place, wouldn't I?

DUTTA: That is right.

SCHWUTTKE: I believe that the surface temperature in general where the focused laser beam hits the silicon surface, there you have the proper temperature that the gas dissociates. There you would get the deposition.

COMMENT: That is pyrolytic.

COMMENT: Would you put up that viewgraph? I also had the same problem.

LANDEL: Also your sketch showed a general budding of the area for the order of associations.

DUTTA: Yes, that is the problem with schematics. They are not very precise. This was to just give an idea of what is going on, but I realize it can be confusing. It is very critical to have the right density of the gas. If you have too high a pressure of gas within your cell, then you get decomposition too early on. As your photons enter the cell you get decomposition very close to the window, and so you have composition all over the walls in the chamber. But if you peak the gas pressure at some critical pressure, and you focus your beam so that the maximum intensity is close to the surface, or at the surface, where you have the absorbed layer, then you dissociate the gas at the surface. You don't have that problem.

TAYLOR: I am having problems, also. Let's assume that you are doing your excitation all very close to the surface but when you undergo a dissociation event the metal atom that is liberated is likely to move in any direction--to be moving straight out away from the surface as frequently as it is moving toward it so, it seems to me like you would get a lot of diffusion through the gas phase before it hit the surface and stuck. Your resolution would not be very good.

DUTTA: Well, apparently once you form your nucleation sites then the sticking coefficient is such that when you are flood-illuminating the substrate, then you have very good localization of the subsequently deposited layer. It sticks very well to those nucleation sites. Are you talking about the initial nucleation?

TAYLOR: No. I can understand if you do your pre-nucleation, that route of preparation, then you have sites to which the deposited atoms can stick, but unless you do that prenucleation, if you are depending on writing a pattern on a substrate without prenucleation, now I think you would have trouble with getting resolution.

DUTTA: Well, people who have not used the prenucleation technique have reported lines of one to two microns with just using the one-shot deposition process.

LANDEL: In this case, you are using a line laser that is focused somewhere off the surface, so you are getting presumably gas-phase disassociation, and then that gives rise to what line? How wide?

DUTTA: Well, with the prenucleated --

LANDEL: No, not prenucleated.

DUTTA: One to two microns.

LANDEL: And how far off the surface are you focusing?

DUTTA: The Bell system researchers don't specify.

LANDEL: I wonder -- in fact, aren't you saying that if you prenucleated, this represents some distance of microns for the pressure you have. You must be dissociating through the whole line, whatever your absorption is, but you must have some recombination rate. So you dissociate and recombine, and only if you have a site close do you have deposition. If you have thought about it, it would seem to me, like Bill (Taylor) said, you are going to have things going off in all directions. And furthermore, it means you are going to have a tremendous loss or wastage of the material you have. It dissociates and now you have the methyl radicals and the metal, and it is just floating around in a cloud, and now it is going to deposit all over the place -- unless one is relying on the dissociation and rapid recombination during the length of the mean free path.

DUTTA: Yes.

QUESTION: Doesn't the intensity at the focal point increase the dissociation?

DUTTA: It does. That is why it is important to have the focus close to the substrate.

COMMENT: You have drawn the laser's focus down at the surface, so that you get more dissociation at the focal point of the laser than back in the gas where it is not so intense.

COMMENT: Plus the fact that it really is a surface-absorbed phase; we are really talking about enormous density gradient too.

LANDEL: Well, it is not clear whether it is dissociation of the surface-absorbed phase, or whether it's dissociation in the gas phase.

COMMENT: The point is, if it is out of the surface-absorbed phase, the density there is much higher than it would be out of the gas phase--3 orders of magnitude or something like that.

COMMENT: I'm getting confused back and forth between prenucleation and the single -- this particular one is the single step process, is that correct?

DUTTA: Well, this is just a generalized viewgraph, depicting the entire technique. I think the prenucleation and the whole technique is just one technique, but a two-step deposition process in which they prenucleate and then flood-illuminate is just breaking down the process into its component parts. I think when you do it one shot, the same thing is happening. The adsorbed layer is being decomposed.

COMMENT: But when done in one shot, this does not represent a flood example, does it?

DUTTA: The localization can be done by either focusing or by using a mask. This was just to generalize the depiction of the technique. I am not specifying how it's being localized.

STEIN: If you look at the second and the third illustrations there, there are wo different functions that the photons are performing. One is, you call it liberating the metal atoms, and the other is actually illuminating the substrate. The way I'm assuming this thing is working is that you've really got to attack that substrate with a laser beam, whether you prenucleate it or whether you just illuminate it. Whether the gas is photolytic or pyrolytic is not as critical as the fact that you've got to get the substrate very receptive to these available atoms that are going to be deposited. I think that's what you're saying. I am not sure; I wish you would correct me. And once you get that substrate ready, then anything close, any atoms close to it, if they are still atoms, are going to stick. Is that what's happening? I mean, you have two functions for that laser beam shown in the second and third photograph. It seems to me that the last function, the bottom one, is the critical one. You've got to illuminate, you've got to prenucleate the surface, to liberate the metal atoms. In fact, you don't want to do much of that away from the substrate.

GALLAGHER: Do you know if anyone has ever made a solar cell and/or laid down metal on a solar cell using this technique?

DUTTA: No.

ZWERDLING: I assume that in this process you have to use wave lengths or photon energies that are capable of breaking the organo-metallic bond. Does that mean you have to choose selected wave lengths for your laser? It is not a thermal process that is breaking the bond and freeing the metal, it is a photolytic process. So you must choose wave lengths, particular wave lengths, for different compounds?

DUTTA: All of the UV wave lengths will do it, some more effectively than others.

ZWERDLING: You're raising the vibrational energy, or the electronic state, to such a point that the vibrations will tear the molecules apart.

DUTTA: That's correct.

LANDEL: You point out that one of the advantages of this was the possibility of having cleaner film. Is there any evidence on whether or not they are cleaner films, than by some other technique? It is a reasonable supposition, but then there are always so many things that can go wrong. Is the supposition borne out in the product?

DUTTA: I think so. The SEM pictures of the deposited films don't show any impurities. It looks very clean, very uniform.