AIP Applied Physics Letters

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Citation: Applied Physics Letters **53**, 1314 (1988); doi: 10.1063/1.100007
View online: http://dx.doi.org/10.1063/1.100007
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Windowless helium lamp assisted chemical vapor deposition of hydrogenated amorphous silicon

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(Received 11 May 1988; accepted for publication 28 July 1988)

A windowless helium lamp is employed to assist chemical vapor deposition of hydrogenated amorphous silicon from disilane feedstock gas at a film growth rate greater than 200 Å/min. Material properties in this preliminary study are comparable to the best hydrogenated amorphous silicon (*a*-Si:H) films produced by conventional bulk plasma CVD techniques. The amount of photoconductivity degradation under long-time illumination is more than plasma-deposited *a*-Si-H thin films. Photoconductivity as high as $\sigma_p = 4\times 10^{-4}$ $(\Omega \text{ cm})^{-1}$ has been obtained.

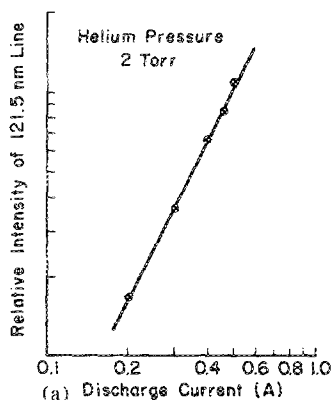
Hydrogen-free amorphous silicon (*a*-Si) films are not suitable for many optoelectronic devices because dangling bonds, which exist in unhydrogenated amorphous silicon, act as efficient trapping and recombination centers.[1,2] Hydrogenated amorphous silicon (*a*-Si:H) containing 3–20% hydrogen, however, is highly photoconductive[3] and it can be doped *n* or *p* type.[4] Hydrogenated amorphous silicon has uses in solid-state optoelectronic devices including solar cells,[3] image transfer surfaces,[5,6] and intermediate structures in other solid-state devices.[7]

The most common method to fabricate hydrogenated amorphous silicon (*a*-Si:H) films is the glow-discharge decomposition of silane[8] gas. The substrate is immersed in the bulk plasma. The glow-discharge electric field (dc,ac,rf) produces hot electrons of 2–10 eV which subsequently collide with and dissociate input feedstock gases. The electron-molecule dissociation products condense on a heated substrate (200–400 °C) and form an amorphous solid. Note that immersion of the substrate in the bulk plasma brings with it ion bombardment of the growing field which can cause film damage, especially to amorphous superlattice structures.[9]

Film deposition using a helium lamp located remote to the substrate offers different molecular dissociation pathways as compared to direct electron impact occurring in the bulk plasma. For example, in the present research, both vacuum ultraviolet photons and excited helium atoms created inside the lamp participate in collisions with disilane molecules to dissociate it. The role of electron impact dissociation is negligible. Although these same photon-molecule and atom-molecule dissociation processes occur in a bulk plasma, they do not dominate over electron impact dissociation.

Photodecomposition of disilane,[10–12] trisilane,[10–12] and also monosilane[13] has been obtained using monoenergetic excimer laser radiation but the photon absorption cross sections are small in the spectral region where excimer lasers operate (157–200 nm).[13] Hence, lasers are employed because of their high photon flux which allows for multiple photon absorption.[14] Broadband vacuum ultraviolet lamp assisted chemical vapor deposition[15,16] and monoenergetic mercury sensitized assisted CVD[17] of disilane to deposit *a*-Si:H thin films have also been reported. In the latter case, excited mercury atoms (Hg*) are used to dissociate disilane in atom-molecule collisions. Disilane has a significant photon absorption cross section in the vacuum ultraviolet (VUV) between 110 and 170 nm.[13] Therefore, a VUV lamp with significant output between 110 and 170 nm could be used for the direct photodeposition of *a*-Si:H thin films.

Conventional VUV lamps use enclosing walls both to confine the discharge and to maintain the required operating pressure. A window is used to extract the plasma generated VUV photons. VUV window materials are very expensive



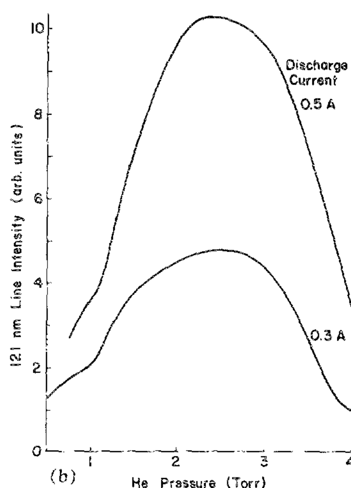


FIG. 1. Dependence of 121.5 nm He II line intensity measured near the substrate: (a) vs lamp discharge current and (b) vs lamp helium pressure.

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and they degrade with prolonged exposure to either moisture or VUV light. VUV entrance windows must also be used on the photo-CVD reactor and undesired film deposits will occur on the inside of the reactor window. Changes in window transmittance vary the intensity of transmitted VUV light from the lamp into the reactor volume and is an undesirable feature.

We utilize an *in situ* VUV helium lamp[18] that is windowless and provides strong VUV light from the He II spectrum as well as a diffusion flux of excited helium atoms (He*). The intensity of He I VUV radiation from the confined helium plasma reaching the remote substrate is low because it is strongly absorbed by the atomic helium ambient via resonant processes. The He II VUV spectrum is propagated far from the confined helium plasma since the ground-state ion and ion metastable density is low outside the confined plasma and absorption is negligible. Both He II VUV photons and He metastable species are used to dissociate Si_2H_6 molecules in the present apparatus via photon-molecule and atom-molecule dissociation processes. The lamp is placed 14 cm from the substrate, so that any plasma electrons are thermalized to room temperature before reaching the substrate. Hence electron impact dissociation plays no role. In summary, a ring-shaped cold cathode generates a well-confined disk-shaped helium discharge that emits both He I and He II VUV line radiation. Due to strong self-absorption by ground-state helium atoms but not ground-state ions, the VUV resonance radiation emitted from the disk plasma spectrum is selectively attenuated as it travels from the lamp to the substrate. This reduces the He I VUV spectrum impinging on the substrate region but not the He II VUV spectrum. For example, strong He II line radiation at 121.5 nm ($4d\,^2D - 2p\,^2P$) was measured in the substrate region by a UV monochrometer (ARC model VM-502), while the He I resonance line at 60 nm was weak. The dependence of the 121.5 nm He II line intensity versus lamp current is shown in Fig. 1(a). Figure 1(b) shows the VUV intensity versus helium pressure. We find, as described below, that the optimum deposition conditions for *a*-Si:H thin-film deposition occur when the 121.5 nm He II line emission is strong suggesting a photodissociation role for 121.5 nm radiation.

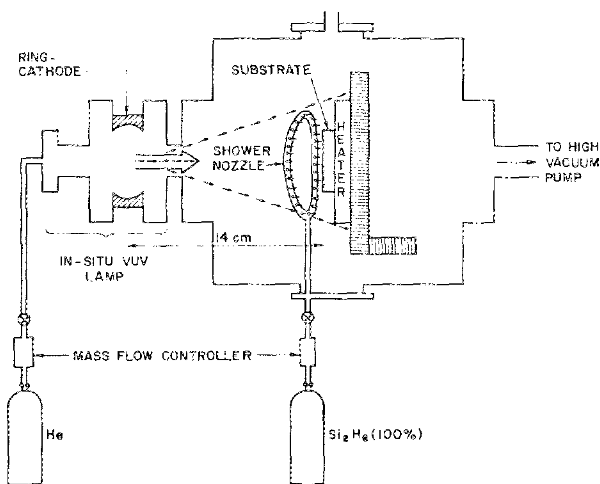

FIG. 2. Schematic diagram of the two-chamber helium lamp-CVD apparatus.

TABLE I. Typical helium lamp-CVD deposition parameters used to form undoped *a*-Si:H thin films.

Energy source (He discharge lamp)	121.5 nm He II line and atomic helium metastables
Current in ring discharge	0.5 A
Voltage on ring discharge	600 V
Donor gas	Disilane (Si_2H_6)
Flow rates of gases used	Si_2H_6, 20 sccm He, 200 sccm
Total pressure	1–1.5 Torr
Substrates	Corning 7059, fused quartz and (100) silicon wafers
Substrate temperature	$50\,^\circ C < T_s < 400\,^\circ C$

The two-chamber deposition apparatus consists of a lamp plasma chamber connected upstream of a remote deposition chamber as illustrated in Fig. 2. Si_2H_6 feedstock gas is introduced into the downstream reactor by a ring-shaped shower nozzle located 1 cm above the substrate as shown in Fig. 2. Helium gas flows through the ring-shaped discharge lamp where it is excited and ionized. Helium afterglow products created in the active discharge flow towards the substrate but only long-lived species such as He($2\,^1S$) and He($2\,^3S$) metastables are judged to arrive at the substrate. The distance between substrate and the VUV lamp is almost 14 cm so excited He* levels, other than metastables, will relax via photon emission before reaching the substrate. He II VUV radiation from the plasma disk lamp also impinges on the substrate as described above. As a consequence the primary dissociation mechanisms of disilane in the apparatus of Fig. 2 are judged to be VUV photodissociation of disilane and disilane-helium metastable ($2\,^1S$ and $2\,^3S$) dissociation reactions. The relative importance of these two dissociation mechanisms is not known at this time nor their changing role versus reactor or lamp conditions.

We used both crystalline silicon wafers and Corning 705 glass as substrate materials for (*a*-Si:H) thin-film depositions using the two-chamber apparatus of Fig. 2. Typical deposition parameters used are listed in Table I. The optical, chemical, and electrical properties of helium lamp assisted *a*-Si:H films have been characterized. The optical parameters of films deposited on transparent substrates were evaluated by conventional transmission spectrophotometry in the $0.3 < \lambda(\mu) < 3.5$ range. The refractive index $n(\lambda)$ and extinction coefficient $k(\lambda)$ of the deposited films have been calculated using the measured T vs λ transmittance spectra using established methods.[10] The calculated refractive index in the nondispersive ($dn/dE = 0$) region was $n = 3.62$. The absorption coefficient $\alpha(\lambda)[=4\pi k(\lambda)/\lambda]$ versus wavelength was also determined. From the $\alpha(\lambda)$ curve we calculated the optical band gap (E_g^{op}) using the Tauc[19] empirical

TABLE II. Material parameters of *a*-Si:H films deposited at 350 °C.

Optical band gap	$E_g^{op} = 1.76$ eV
Refractive index	$n = 3.62$
Hydrogen concentration	$C_H = 4.3\%$
Photoconductivity (AM1 100 mW cm^{-2})	$\sigma_p = 4\times 10^{-4}\ (\Omega\ \mathrm{cm})^{-1}$
Dark conductivity	$\sigma_d = 3.5\times 10^{-9}\ (\Omega\ \mathrm{cm})^{-1}$
Conductivity activation	$E_a = 0.71$ eV

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TABLE III. Comparison of material properties of undoped a-Si:H films deposited with different techniques.

	Laser CVD			Lamp CVD			He lamp CVD
σ_{ph} (AM1)	1.2×10^{-5}	2×10^{-4}	2×10^{-6}	10^{-5}	10^{-5}–10^{-4}	6×10^{-4}	4×10^{-4}
σ_D	2.5×10^{-11}	2×10^{-9}	1×10^{-10}	10^{-10}	10^{-11}–10^{-10}	4×10^{-9}	3.5×10^{-9}
Donor gas	Si_2H_6	Si_2H_6	Si_2H_6	Si_2H_6 Si_3H_8	Si_2H_6	Si_2H_6	Si_2H_6
Energy source	193 nm excimer laser	193 nm excimer laser	193 nm excimer laser	184.9 nm	253.7 nm Hg sensitized	254 nm + weak 185 nm no Hg	121.5 nm He II line & atomic helium metastables
Deposition rate	200–300 Å/min	2 Å/s	100–200 Å/min	0.1 Å/s	2 Å/s	15 Å/min	200 Å/min
Reference	10	11	12	15	17	16	Present Work

relation. The extrapolated value of $(\alpha E)^{1/2}$ vs E yields an E_g value for our a-Si:H film of $E_g = 1.76$ eV.

Fourier transforms infrared (FTIR) spectroscopy was used to identify both the total hydrogen content and the form of the silicon-hydrogen molecular structure. Hydrogen-silicon bonding was found to be predominately in the Si-H stretching mode for all the a-S:H films deposited over the entire range of substrate temperature investigated. The Si-H hydrogen concentration was found to vary from 4 to 8% as the substrate temperature varied from 350 to 300 °C.

Electrical conductivity of the deposited films was measured in the dark (σ_d) and also under illumination (σ_p) using an AM1 (100 mW cm^{-2}) lamp. In this measurement we employed the coplanar electrode configuration using two parallel Ag electrodes for electrical contacts. The σ_p/σ_d ratio was measured to be 1.1×10^5. The temperature variation of the dc electrical conductivity $\sigma(T)$ versus inverse measurement temperature (Arrhenius plot) determined the activation energy for conductivity to be $E_a = 0.71$ eV for a film deposited at a substrate temperature of $T_s = 350$ °C and $E_a = 0.9$ eV for a film deposited at a substrate temperature of $T_s = 300$ °C. The activation energy decrease is primarily due to the decreasing content of hydrogen in the deposited film resulting in a lower value of energy gap. Detailed material parameters of deposited films at substrate temperature of $T_s = 350$ °C are summarized in Table II.

Deposited a-Si:H films under illumination for extended periods of time display a decrease of both photoconductivity and dark conductivity as reported by Staebler and Wronski.[20] Changes of spin density[21] and infrared absorption[22] have also been observed. We also examined the influence of long-time illumination on the steady-state photoconductivity for a deposited film at $T_s = 350$ °C using the helium lamp. Photoconductivity before light soaking was $\sigma_p = 4\times10^{-4}$ $(\Omega\,\text{cm})^{-1}$ while after a 24 h AM1 light exposure the measured photoconductivity dropped to $\sigma_p = 2.9\times10^{-6}$ $(\Omega\,\text{cm})^{-1}$. This final value is ten times less than the best results for plasma-deposited a-Si-H thin films. Subsequently we annealed the sample in a N_2 environment at $T = 170$ °C for 1 h and the measured photoconductivity was $\sigma_p = 9\times10^{-4}$ $(\Omega\,\text{cm})^{-1}$. A comparison between a-Si:H film properties deposited with the helium lamp method and with other photo-CVD methods is summarized in Table III. In all cases Si_2H_6 feedstock gas was used. We are presently depositing a-Si:H thin films using both H_2 and He lamps with silane and disilane feedstock gases to compare results to those described herein.

In summary, we have demonstrated a new method to deposit a-Si:H thin films using VUV photon and atomic metastable dissociation of disilane gas. Helium lamp assisted CVD of hydrogenated amorphous silicon provides material properties comparable to conventional plasma CVD methods. Stability of the deposited films does not deteriorate drastically after long-time photon illumination.

This research was supported in part by the Defense Advanced Research Projects Agency, Applied Electron and the Naval Research Laboratory.

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