

Laser-induced structural changes in magnetron-sputtered hydrogenated microcrystalline silicon films

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Hydrogenated microcrystalline silicon films were prepared by the rf magnetron-sputtering technique and structurally characterized by Raman spectroscopy, transmission electron microscopy, x-ray diffractometry, and infrared vibrational spectroscopy. The effects of variations of laser power and wavelength (and therefore energy) of incident radiation on the structure of hydrogenated microcrystalline silicon films were systematically studied by Raman scattering and transmission electron microscopy (TEM). With the increase in laser power, a phonon softening of the TO-like peak from 516 to 490 cm^{-1} was observed, followed by a reversal of the trend with a further increment in laser power. TEM studies clearly revealed an increase in the amorphous phase for laser exposure in the power range where phonon softening was observed with subsequent enhancement in crystallinity for still higher powers.

I. INTRODUCTION

Laser-induced structural modifications in hydrogenated amorphous silicon films have evoked considerable interest both from the point of view of understanding fundamental kinetics¹ and also from the aspect of producing conducting films for device applications.² Binary Si:H materials are usually fabricated by the rf-glow-discharge technique,^{3,4} photochemical vapor deposition,^{5,6} and sputtering.^{7,8} With proper parametric variations, hydrogenated microcrystalline silicon films ($\mu\text{c-Si:H}$), structurally different from the conventional $a\text{-Si:H}$ can be fabricated by each of these processes.⁹⁻¹¹ With higher conductivity and lower visible-range absorption as compared to $a\text{-Si:H}$ films, $\mu\text{c-Si:H}$ has become an important electronic material. It is well known that a narrow crystallinelike peak at frequencies marginally lower than 520 cm^{-1} , in Raman-scattering experiments, indicates the growth of microcrystals.¹² An unusually large shift from the crystallinelike mode was observed by us in some magnetron-sputtered $\mu\text{c-Si:H}$ films, with the peak position moved to 500 cm^{-1} .¹³

The present work is a systematic follow-up of that initial observation. $\mu\text{c-Si:H}$ films were chosen at random to cover a range of volume fraction of the microcrystalline phase. The films were subjected to successive laser exposures with variations in wavelength and power. The structural modifications were monitored at each stage by Raman-scattering experiments and transmission electron microscopy (TEM). An initial enhancement of disorder followed by laser-induced crystallization were observed in $\mu\text{c-Si:H}$ films for the first time. An explanation of the phenomena is offered.

II. EXPERIMENT

$\mu\text{c-Si:H}$ films were prepared by a planar magnetron-rf-sputtering technique. A hard-pressed poly-Si target

(20.9-cm diameter) was sputtered by a mixture of argon and hydrogen. The hydrogen flow rate R_H was varied from 70% to 90% with the total flow rate maintained at 100 standard cm^3/min . The substrate to target distance was fixed at 7.3 cm, the system pressure during sputtering was fixed at 30 mTorr, and the power density was fixed at 1.8 W/cm^2 . The substrate temperature was typically 220 $^\circ\text{C}$.

Films were checked for microcrystalline phase by x-ray diffractometry (Phillips x-ray generator PW 1130 and diffractometer PW 1710 with $\text{Cu K}\alpha$ radiation). Raman-scattering experiments were performed using a continuous-wave argon-ion laser ($\lambda=514.5, 488.0$ nm) and the laser power was varied from 50 to 500 mW. A double monochromator and photon-counting electronics completed the setup. Transmission electron microscopy studies were done using a JEOL-200 CX microscope operating at 160 kV. TEM samples were exposed to the Ar-ion laser ($\lambda=514.5$ nm) for 20 min at 100, 300, and 440 mW, respectively. Secondary-ion-mass spectrometry (SIMS) depth profiles of Si^+ , SiH^+ , and H^+ were taken in a VG 12-12S SIMS system prior to and after laser exposure. The bonded hydrogen content of selected films was determined from infrared vibrational spectroscopy.

III. RESULTS

Figure 1 shows the x-ray-diffraction patterns of $\mu\text{c-Si:H}$ films for variation in the hydrogen flow rate. For $R_H=70\%$, the peak characteristic of the (111) orientation of crystalline silicon powder is only evident. With increasing R_H , (220) and (311) orientations of silicon develop in addition to the (111) peak. The bonded hydrogen content in these films as calculated from the wagging mode of Si-H vibration varies roughly from 3 to 6 at. %.

Figure 2 shows the Raman-backscattering spectra of a $\mu\text{c-Si:H}$ film taken at different powers and wavelengths in the sequence (a)-(f), the x-ray-diffraction pattern of

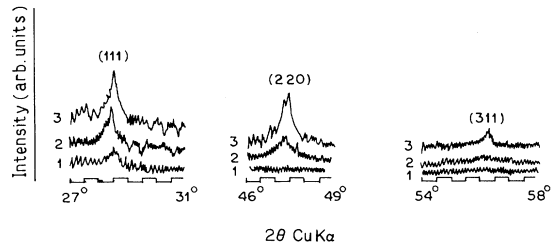


FIG. 1. X-ray diffraction patterns of μc -Si:H films deposited at different hydrogen flow rates (R_H). Curve 1, $R_H=70\%$; curve 2, $R_H=80\%$; curve 3, $R_H=88\%$.

which is represented by curve 3 of Fig. 1. For $\lambda=514.5$ nm, as the laser power P is raised from 100 to 300 mW, the peak position of the TO-like mode shifts from 516 to 500 cm^{-1} with a concurrent increase in the full width at half maximum (FWHM) [Figs. 2(a) and 2(b)]. By decreasing λ to 488 nm the phonon softening is more prominent [Figs. 2(c) and 2(d)] with the peak shifting to 490 cm^{-1} for $P=200$ mW. For $P=300$ mW, a marginal peak shift toward higher frequency is observed [Fig. 2(e)]. However, for $P=500$ mW, the Raman-backscattering spectrum [Fig. 2(f)] is similar to the one shown in Fig. 2(a), with the peak frequency of the crystalline component approaching the characteristic 520 cm^{-1} position.

Table I summarizes data from Raman-scattering experiments for selected samples with different volume fractions of the microcrystalline phase. The latter were calculated from the spectra obtained for $\lambda=514.5$ nm and $P=100$ mW. The deconvoluted linewidth is represented by W_T . A shift of the crystalline component frequency to a lower wave number and increase in W_T , with the increase in P , is a common feature for both the representative samples. As seen in Fig. 2, here too the effect is more pronounced when $\lambda=488.0$ nm is used. For $P \geq 300$ mW, however, the trend is reversed. For $P=500$ mW or even for $P=50$ mW after exposure at 500 mW, the peak frequency again approaches the 520-cm^{-1} position with a marked decrease in W_T .

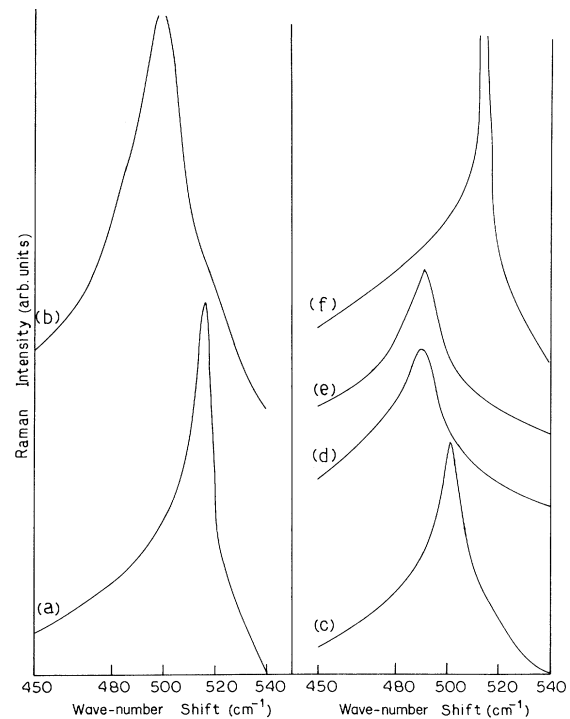


FIG. 2. Raman-backscattering spectra (of 4880- and 5145-nm excitation) of μc -Si:H film taken at different laser powers. Curve (a), $\lambda=514.5$ nm, $P=100$ mW; curve (b), $\lambda=514.5$ nm, $P=300$ mW; curve (c), $\lambda=488$ nm, $P=50$ mW; curve (d), $\lambda=488$ nm, $P=200$ mW; curve (e), $\lambda=488$ nm, $P=300$ mW; curve (f), $\lambda=488$ nm, $P=500$ mW.

The bright-field TEM image and the transmission electron diffraction (TED) pattern for films deposited with $R_H=80\%$ are shown in Figs. 3(a) and 3(b), respectively. The microcrystalline nature is obvious with a uniform distribution of crystalline regions of $40\text{--}60\text{ \AA}$ studded with larger zones, $200\text{--}600\text{ \AA}$. Laser exposure with $P=100$ mW ($\lambda=514.5$ nm) does not reveal appreciable

TABLE I. Results of Raman-scattering studies of magnetron-sputtered μc -Si:H films.

Sample No.	λ (nm)	P (mW)	Peak position (cm^{-1})	W_T (cm^{-1})	Volume fraction (%)
1	514.5	100	516	8	42
	514.5	300	500	20	
	488.0	50	502	16	
	488.0	100	494	20	
	488.0	200	490	20	
	488.0	300	492	16	
	488.0	500	515	8	
2	514.5	100	514	8	33
	514.5	300	500	20	
	488.0	100	503	12	
	488.0	200	492	20	
	488.0	300	495	16	
	488.0	400	496	16	
	488.0	50 ^a	510	12	

^aAfter exposure at 500 mW.

structural changes [Figs. 3(c) and 3(d)]. However, for $P=300$ mW, enhancement of the amorphous zone is clearly evident from the bright-field TEM image. The smaller crystals seem to be replaced by a disordered matrix. However, the number density of larger crystalline zones appears to increase at the same time. These [Fig. 3(e)] are scattered in an essentially amorphous matrix. With further increase in laser power ($P=440$ mW) the enhancement in crystallinity is evident from both the

TEM image and the TED pattern [Figs. 3(g) and 3(h)].

SIMS depth profiles of Si^+ , SiH^+ , and H^+ for unexposed and laser-exposed $\mu\text{c-Si:H}$ films were taken. From Table II, the relative decrease in SiH^+ and H^+ after laser exposure is evident, more so on the top surface of the film.

IV. DISCUSSION

It has been shown before that the dominant effect of a sufficiently powerful laser pulse consists in heating of the

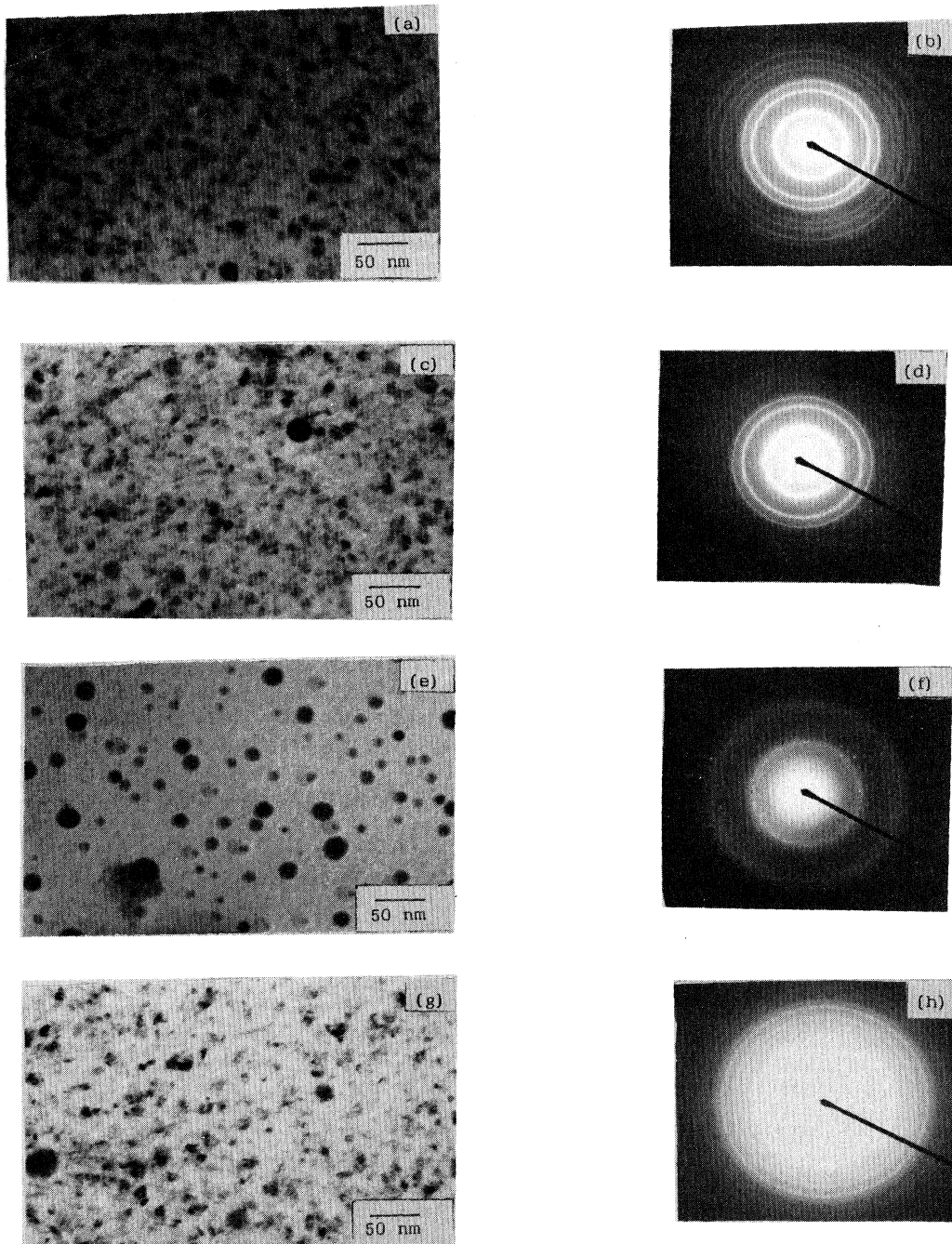


FIG. 3. Bright-field TEM image and corresponding TED pattern of $\mu\text{c-Si:H}$ film, for $R_{\text{H}} = 80\%$, laser exposed at different powers ($\lambda = 514.5$ nm) for 20 min. (a) and (b) as deposited (without any exposure), (c) and (d) for $P = 100$ mW, (e) and (f) for $P = 300$ mW, (g) and (h) for $P = 440$ mW.

TABLE II. Results from SIMS depth profile studies on unexposed and laser-exposed $\mu\text{c-Si:H}$ films. Counts have been normalized with respect to Si^+ .

Position	Unexposed (A)			Exposed (B)			A/B	
	Si^+	SiH^+	H^+	Si^+	SiH^+	H^+	SiH^+	H^+
Top surface	1	3×10^{-1}	5×10^{-3}	1	1.8×10^{-1}	2.5×10^{-3}	1.7	2.0
Bulk	1	1.9×10^{-1}	2.3×10^{-3}	1	1.7×10^{-1}	1.7×10^{-3}	1.1	1.4

semiconductor.¹⁴ Again, a shift in the optical-mode frequency from 525 to 510 cm^{-1} in silicon had been reported,¹⁵ with the increase in sample temperature from 20 to 770 K. There is a concomitant increase in the linewidth. In the present study, increase in laser power P and decrease in the wavelength of incident light λ lead to effects similar to but more pronounced than that of heating in the active volume of the sample.

The decrease in the peak frequency of the crystalline component and the increase in the deconvoluted linewidth had been attributed to a decrease in the crystallite size¹² coupled with an increase in disorder at the boundaries of the crystallites. In the case of our samples, higher P or lower λ may be responsible for breaking weak Si—Si bonds at the boundaries of microcrystals and thus inducing disorder. $\mu\text{c-Si:H}$ is different from the usual compact $\alpha\text{-Si:H}$ network, as it consists of regions distinct from each other—the crystalline zone, grain boundary region, and defective amorphous region. The laser-induced effect is therefore different in the different regions. TEM micrographs in Fig. 3 testify to this. In stronger crystalline zones, crystallinity could be enhanced, while side by side there could be a depreciation in the other phases, and the net effect depends upon the initial zonal distribution. For sufficiently high laser power, however, laser-induced crystallization is evident from both Raman-scattering experiments as well as TEM studies. The local heating at high P also could be responsible for partial hydrogen evolution. SIMS studies point toward this. However, it can help only in grain growth by minimizing the hindrance effect of passivating hydrogen¹⁶ and therefore does not contradict experimental observations.

V. CONCLUSIONS

Laser-induced structural modifications in heterophase $\mu\text{c-Si:H}$ films have been reported. An initial enhancement of disorder with an increase in laser power followed by laser-induced crystallization in magnetron-sputtered $\mu\text{c-Si:H}$ films has been observed and presented. A shift in the peak of the TO-like mode from 516 to 490 cm^{-1} with a concomitant increase in linewidth has been observed in a specific case. With a subsequent increase in laser power, the peak position has been found to return to 515 cm^{-1} with a decrease in the linewidth. TEM studies have given supporting evidence for an initial creation of disorder followed subsequently by an enhancement of crystallinity.

The breaking of weak Si—Si bonds has been cited as one of the reasons for an increment in disorder. In the region of the subsequent augmentation of crystallinity, it has been found from SIMS studies that the necessary laser power could cause sufficient sample heating so as to induce partial hydrogen evolution. This would only be helpful in grain growth.

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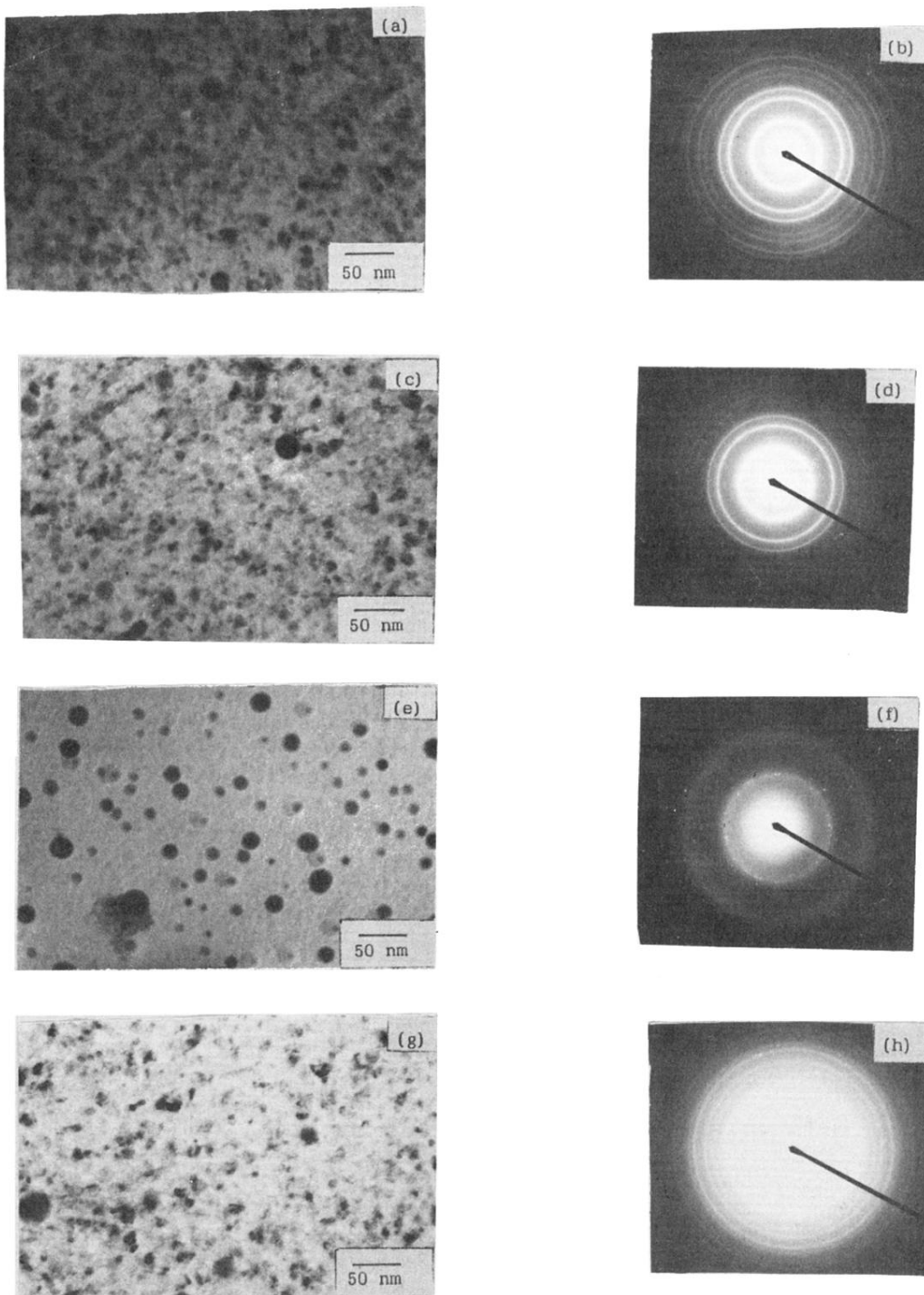


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