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Low-temperature polysilicon deposition by ionized magnetron sputtering

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Ionized magnetron sputtering was successfully applied to polycrystalline silicon thin-film deposition on glass substrate at temperatures lower than 250 °C maintaining a deposition rate of about 133 Å/min. Hydrogen mixing was effective up to Ar:H₂=10:6 by mass flow rate. Prior to deposition, H₂ inductively coupled plasma was used for precleaning the substrate with -40 V bias. During Si deposition, the substrate biasing scheme was in two steps; +20 V for an initial stage and +20 to -40 V bipolar pulse bias for the rest of the deposition time. The crystallinity was evaluated by both x-ray diffraction analysis and Raman spectroscopy; the average crystalline fraction was calculated as 70%. Grain size was measured in plan-view scanning-electron micrographs after selective etching of the amorphous phase by chemical solution. In 800-nm-thick samples, grains are 500–700 Å in diameter. Optical emission spectroscopy was used as real-time diagnostics, and ionization of sputtered silicon atoms distinctly increased as the hydrogen partial pressure increased. The successful deposition of polycrystalline silicon was explained as being due to enhanced ionization of sputtered and reflected neutrals and resultant energy control by bipolar substrate bias. © 2000 American Vacuum Society. [S0734-2101(00)13104-5]

I. INTRODUCTION

The thin-film transistor/liquid-crystal display (TFT/LCD) industry has been experiencing a need for finer display capability and higher charge-carrier mobility necessary in large-area projection devices. Currently, laser-annealed polycrystalline silicon is used, but postannealing of plasma-enhanced chemical vapor deposited (PECVD) amorphous silicon (*a*-Si) requires high-power excimer laser recrystallization and has inherently low throughput. The cost is still high for mass production, and adsorbed gases during CVD will explode during high-power laser scanning to make blisters in addition to a rough surface. A new deposition technology for direct polycrystalline silicon should have manufacturability and high crystallinity. In CVD, mixed gases of SiH₄ and H₂ are used in PECVD for depositing poly- or microcrystalline Si film on various substrates such as quartz, glass, and single-crystalline silicon. Recently, Murata *et al.* reported that a two-step process could increase the crystallinity of the Si film at the fairly low substrate temperature of 300 °C.¹ They maintained a very slow deposition rate of 0.2 Å/s at the initial nucleation stage, equivalent to one-tenth of the total film thickness, and made a charge-free state by installing strong magnets in front of a substrate. In the following step, normal electron cyclotron resonance PECVD was used. The idea of applying a magnetic field in a large-area deposition machine will not be easily realized; and CVD uses toxic or explosive gases such as SiH₄ that are not environmentally friendly. In the magnetron sputtering arena, Yang and Abelson reported that polycrystalline silicon with a mean grain diameter of ~400 Å was successfully deposited on a 100-Å-thick microcrystalline hydrogenated silicon seed layer.² They also performed a kinetic study of incoming fluxes toward a substrate in a reactive magnetron sputtering process; fast

neutral hydrogen atoms both implant and recoil, releasing surface H.³ In a heavily ionized process, such as pulsed laser ablation, there was a report from Trusso and Vasi;⁴ in appropriate hydrogen partial pressure, polycrystalline Si film was successfully deposited on a glass substrate, which means depositing ions with kinetic energy of several eVs that should assist the adatoms to crystallize without creating severe damage. In reactive magnetron sputtering of damage-sensitive materials, where fast reflected neutrals (~100 eV) cause damage, we can control their energy either by ionizing and retarding with positive substrate bias, or by collision slowdown in high background gas pressure. In this study, we applied an ICP-based ionized magnetron sputtering method to deposit polycrystalline Si on glass substrate, where relatively high gas pressure (>4 Pa) is used for efficient ionization of sputtered neutrals by electron-impact collisions. Ionization of depositing atoms (like Si) and proper acceleration would increase the adatom's surface mobility so that crystallization at low temperature becomes easier. It is very interesting that in high-density plasmas, the angular distribution of incoming ions has some correlation with defect formation and enhanced crystallization. The balance between those two processes can be steered by energy control of the incoming particles. The benefit from the ion-assisted deposition process results from: (1) the parallel component of the incoming particle's momentum that is induced either from collisions in a substrate sheath, or (2) succeeding elastic collisions with adatoms present on the substrate surface, where the transferred energy should be lower than the minimum lattice displacement energy of the growing film surface. In the case of using an ion gun, the incident angle determines this effect; in a plasma-immersed process, this occurs because of the gas pressure. For an example, the above (Trusso and Vasi) reports that laser ablation of silicon deposits poly-Si on a glass; most of the depositing particles are ionized by high-power

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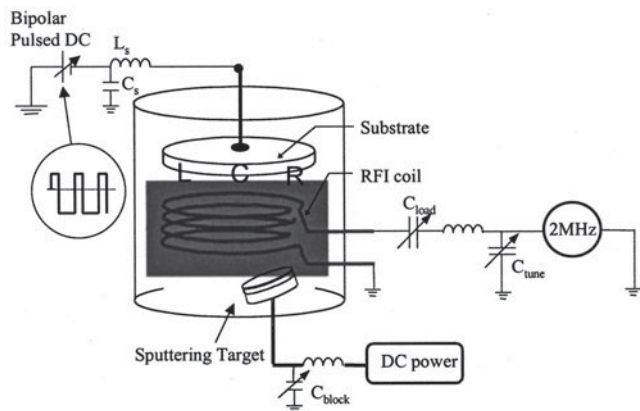


FIG. 1. Experimental setup. ICP is powered by a 2 MHz, 2500 W generator, and sputtering is done by dc power supply. The substrate biasing voltage is generated at square pulse signal generator (max. 10 V_{pp}) and fed into a bipolar op-amp, where it can be amplified in the range of -100 to +100 V and also has variable dc offset. During pretreatment, a continuous -20 V is supplied, and in an initial stage of deposition, +20 V, and during main deposition stage, +20 V (25% duty) and -40 V (75% duty) of bipolar pulsed voltage is used for biasing.

laser absorption, and the background gas pressure is as high as 88.6 Pa. So the depositing particles should have highly randomized angular distribution, where the perpendicular momentum component effectively enhances the adatom's mobility. In this study, we used two strategies: one is to use high gas pressure and the other is to use bipolar pulse bias of the substrate to cause the incoming ions to relax their directionality by oscillating the sheath at several tens of kHz. We expect that fast reflected neutrals should be slowed down either by high gas pressure or ionization, followed by appropriate substrate bias; depositing atoms of Si should be ionized and accelerated to optimal energy for low-temperature crystallization on the substrate surface.

II. EXPERIMENTAL METHOD

Figure 1 shows our ionized magnetron sputtering system: a 50-mm-diameter magnetron cathode, and a 250-mm-

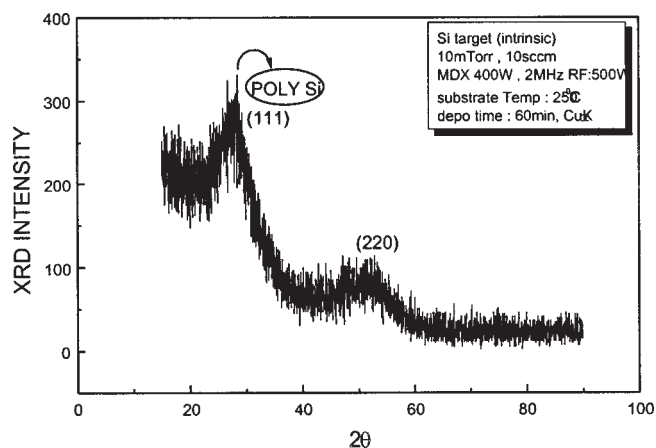
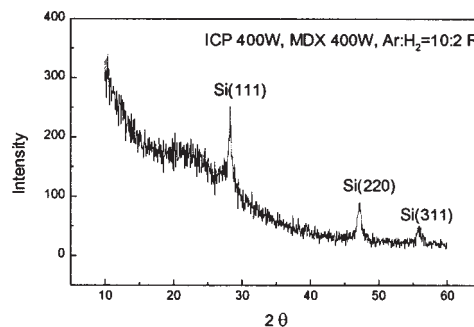
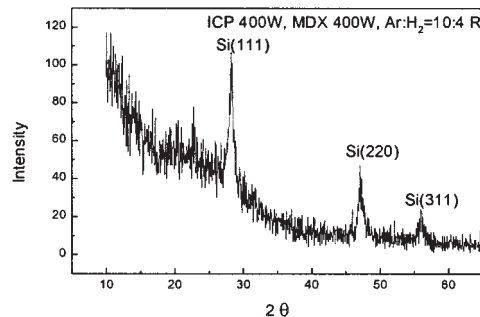


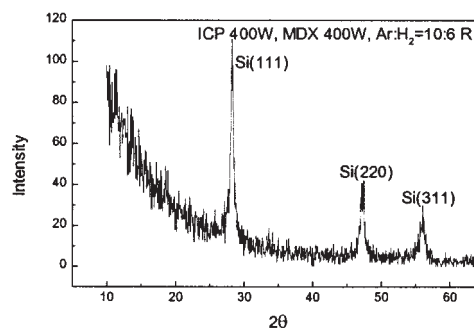
FIG. 2. X-ray diffraction data show microcrystalline Si is deposited with ICP sputtering in pure Ar environment (sputtering power dc 400 W; ICP 2 MHz, 500 W, 1.33 Pa, 250 °C, 60 min).



(a)



(b)



(c)

FIG. 3. X-ray diffraction results show that addition of hydrogen into sputtering gas environment enhanced crystalline-silicon formation during deposition (250 °C, 60 min, sputtering dc 400 W, ICP 2 MHz, 400 W, +20–40 V bipolar pulsed substrate biasing), (a) Ar:H₂=10:2, (b) Ar:H₂=10:4, (c) Ar:H₂=10:6.

diameter, four turn, inductively coupled plasma-generating coil are installed in a 380-mm-diameter stainless-steel chamber. Substrate biasing power is supplied by a pulse signal generator, a bipolar operational amplifier (Kepco, BOP™-100-1M), with a low-pass filter unit to cut off interference from a 2-MHz-ICP power source (ENI, GMW-2500™, 2500W). The pulse width can be varied from a few ns to ms, and the repetition rate can be increased up to 18 kHz. A substrate made of conventional soda-lime glass was positioned 120 mm above the Si target, and the temperature was controlled from room temperature to 400 °C by a resistive heater block. High-purity gases (99.999%) of Ar and H₂ are introduced through a gas dose ring with small holes (0.8 mm diameter) on the top surface. The chamber was evacuated to

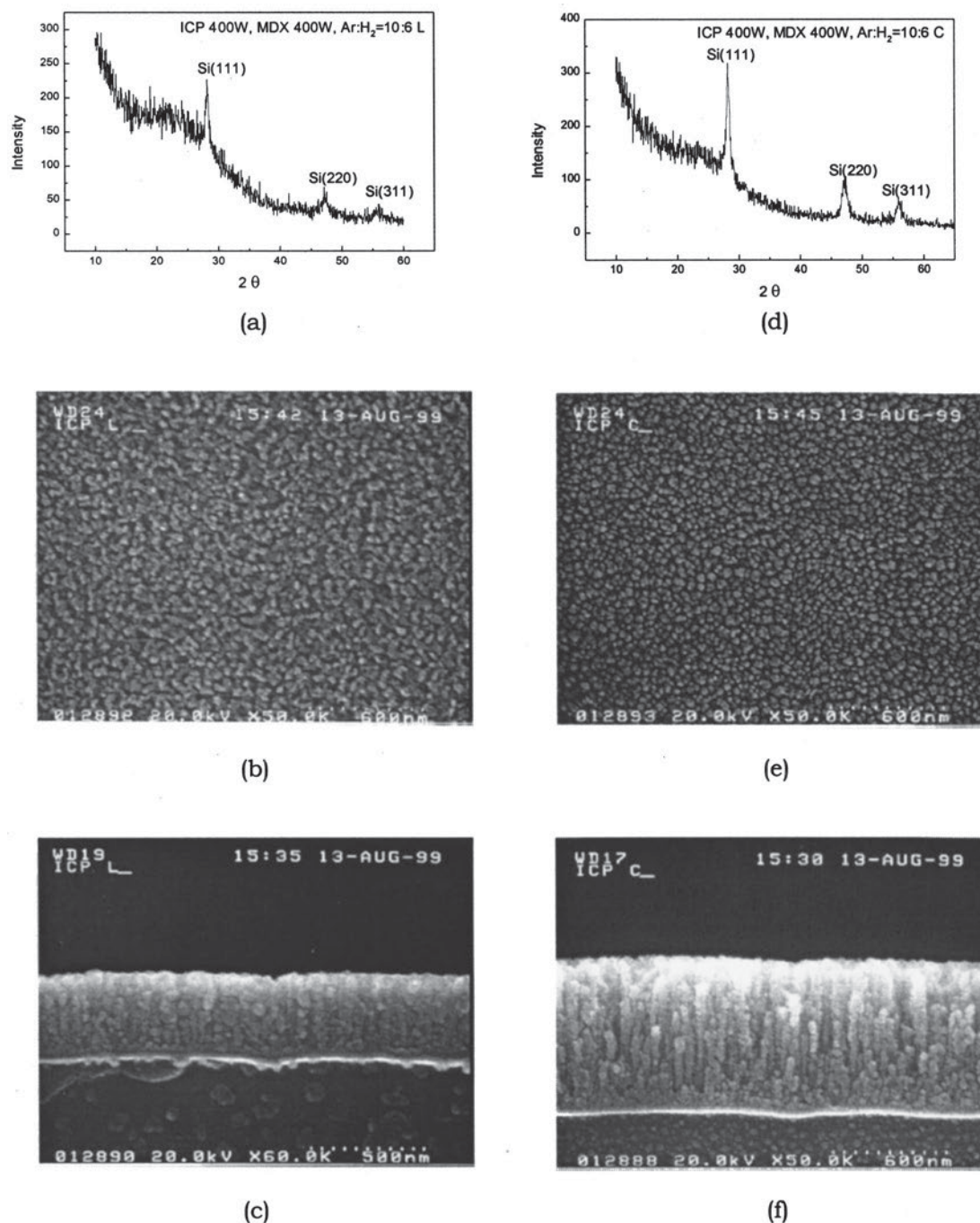


FIG. 4. X-ray diffraction analysis and SEM micrograph show that films have good structural property and grain size from 300 to 700 Å. (a), (b), and (c) are deposited in high- Ar^+ bombardment condition, and (d), (e), and (f) are deposited in low Ar^+ bombardment condition.

about 2.66×10^{-4} Pa by a turbomolecular pump (Alcatel, 5400CP™, 400 L/s) and baked at 150 °C for about 1 h. Prior to main deposition, hydrogen discharge cleaning using ICP was done for 20 min with a negative bias of -40 V. In the deposition stages, +20 V bias was applied for 10 min and switched to bipolar pulse bias (+20 V to -40 V) continuously. Deposited samples were investigated by x-ray diffraction analysis (Bruker analytical, D-5005RA™, 18 kW rotating anode, $\text{Cu K}\alpha$). To observe the grain structure by scanning electron microscopy, the amorphous phase was se-

lectively etched away by a chemical solution. Grain size distributions were measured by software developed by Leica (Q-win™), and Raman spectroscopy was done in a micro-Raman system using a 632.8-nm-He-Ne laser (Renishaw, System-2000™). The factors that affect the crystallinity and structural properties were investigated: substrate temperature, hydrogen mixing ratio, ratio of ICP to sputtering power, thickness, substrate bias, and total pressure. Crystalline fraction was determined from Raman spectroscopy data after decoupling of the amorphous and crystalline peaks by Lorent-

zian fit.⁵ As a real-time plasma diagnostic, optical emission spectroscopy over the plasma volume was done through a quartz view port by an optical fiber and a CCD detector (Ocean optics, SQ-2000™).

III. RESULTS AND DISCUSSION

A. Effects of hydrogen mixing

Sputtered silicon in an Ar gas background only produced amorphous or nanocrystalline Si film at a moderate temperature range (less than 500 °C). This was the same for ionized physical vapor deposition (I-PVD), as shown in Fig. 2. The ICP power and some other process variations were tried, but in most cases, they gave only poorly crystalline film. In this study, hydrogen mixing was tried by varying the mass flow ratio of Ar and H₂ from 10:2 to 10:10. Total pressure changes from 4 to 4.4 Pa, respectively, and this change is not believed to change the slowdown distance of the fast neutrals significantly. In Fig. 3, the x-ray diffraction data show that the mixing ratio of Ar:H₂=10:6 is optimal in depositing polycrystalline silicon film. Mota *et al.* report that the origin of hydrogen mixing effects are that the dangling bonds between Si and Si are reduced, based on interatomic potential calculation.⁶ The halo centered around $2\theta=22^\circ$ appears to be from the glass substrate. A broad band from the amorphous Si phase is reported to be around $2\theta=30^\circ$. In our experimental setup, the substrate and target surface is inclined about 15°, and in each run, three slide glasses are positioned at the substrate holder, where three different samples (left, center, and right position) were made at different distances from the target; so, they had different thicknesses and bombarding ion flux compositions (i.e., Ar⁺ and H₂⁺). In the L position, Ar⁺ is the main bombarding species; but in the R position, the portion of Ar⁺ should be decreased, with a lower deposition rate of silicon. As noted earlier, fast neutrals such as hydrogen atoms are believed to break Si–H bonds on the surface and make them desorb as a form of H₂. As conventional magnetron sputtering is done in gas pressure lower than 0.2 Pa reflected neutrals fly a few centimeters to a substrate, which is not enough distance to slowdown to room-temperature neutrals. As I-PVD is done in relatively high gas pressure of 5 Pa or higher, the fast neutrals must be slowed down first, and some of them are ionized by an electron impact collision or a Penning process. Substrate biasing

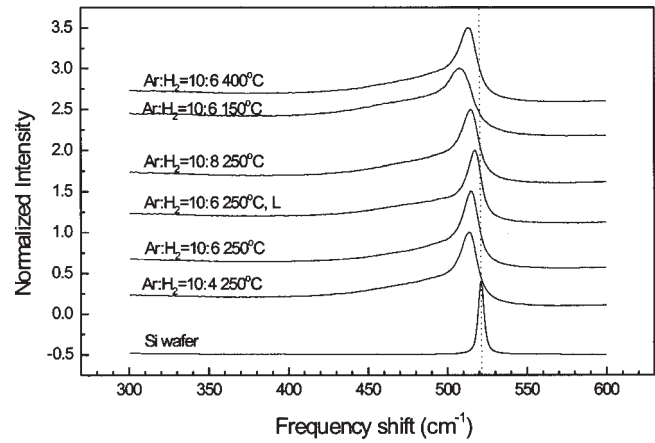


FIG. 5. Raman spectroscopy measurements show that optimal hydrogen mixing ratio is around Ar:H₂=10:6, and heating up to 400 °C does not show much improvement compared to case of 250 °C.

can change the incoming particles energy distribution significantly. In the present study, a bipolar pulse bias scheme was used to solve the charging of the insulating substrate and to control the incoming ion's energy. Energy-selective quadrupole mass spectrometry is planned for future study to confirm this hypothesis.

B. Grain-structure observation

To measure the crystalline fraction and the grain size, the amorphous phase in the deposited specimen was selectively etched by a chemical solution. In Fig. 4, the plan view of samples deposited in Ar:H₂=10:6 at different positions reveals well-developed polycrystalline silicon surfaces. The sample in Fig. 4(a) has a grain-size distribution of about 300–500 Å, and Fig. 4(b) has a grain-size distribution of about 300–700 Å. The fraction of bright crystalline area was measured by an image analysis program, and the average result was about 73%. From the cross-sectional views, normal columnar structure appeared, and there was no abrupt change in microstructure between the the initial stage and the main deposition stage. The positive bias of +20 V in initial nucleation stage on crystalline formation is thought to be due to the effective kinetic energy control in high-density multi-component plasma, i.e., Ar, H, H₂, Si, and their ions. As mass spectrometric study is scheduled, the plasma species in

TABLE I. Crystalline fraction calculated from Raman data with $y=0.9$ in $I_c/(I_c+yI_a)$ after deconvolution with Lorentzian fit.

Specimen i.d.	Deposition conditions		<i>a</i> -Si peak area	<i>c</i> -Si peak area	Crystalline fraction (x_c)	<i>c</i> -Si position (cm ⁻¹)
	Ar:H ₂	T_{sub} (°C)				
990809a-R-2	10:4	250	2.6904	8.1074	0.77	513.6
990809b-C	10:6	250	3.1983	6.393	0.69	515.6
990809b-L	10:6	250	1.2396	2.8873	0.72	517.8
990810a-C	10:8	250	1.7088	2.1867	0.58	514.6
990811a-C	10:6	150	1.0645	2.3799	0.71	508.3
990821a-R	10:6	400	2.2426	6.4447	0.76	513.6

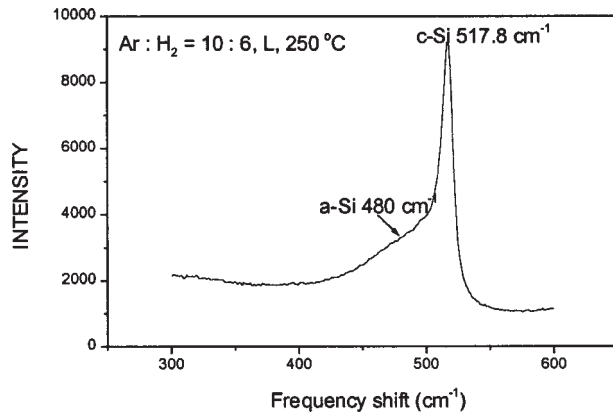


FIG. 6. Extended scan of Raman spectroscopy. Crystalline peak is shifted from 520 to 517.8 cm^{-1} and also contains amorphous Si contribution around low-frequency shoulder.

the ICP volume will be clarified, and we will confirm the results by OES. As for the ion energy distribution in I-PVD, Kusano *et al.* measured the ion kinetic energy in a metal sputtering system.⁷ In this study, Ar^+ and Ti^+ have peak energy higher than 150 eV with zero termination resistance of the ICP coil (as in our study), whereas Ti^+ has a broader peak than Ar^+ . They used an unshielded metal antenna that draws a large electron current to the ground that induces large negative coil potential but in our study, the Cu tube antenna was shielded from plasma by an insulating material, so the plasma potential should not be as high as in their case.

C. Raman spectroscopic measurements

In Fig. 5, the frequency shift in Raman spectroscopy represents crystallinity, and the crystalline fraction can be deduced. A sample deposited at 150 °C showed a broad amorphous band around 480 cm^{-1} , and the crystalline peak was also shifted toward 500 cm^{-1} . As a reference, the Raman shift of a silicon wafer was measured and gave a sharp peak at 520.4 cm^{-1} . Considering the peak between 500 and 520 cm^{-1} as a crystalline silicon peak, the crystalline fraction can

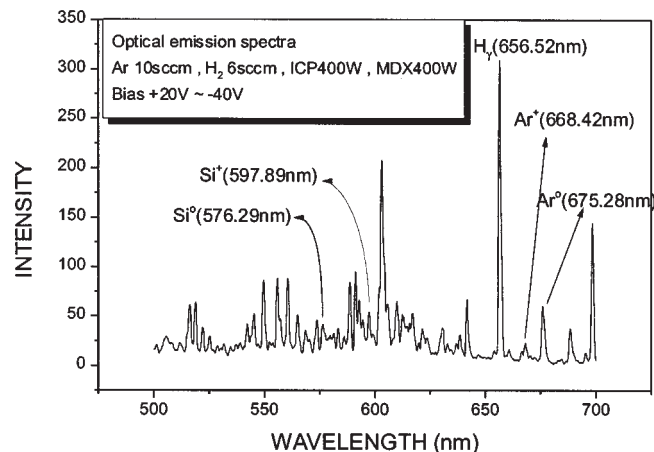
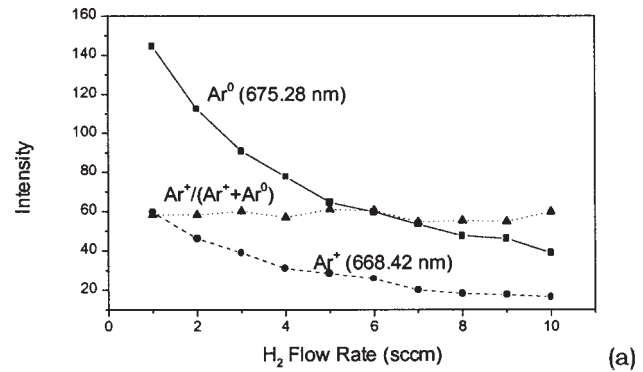
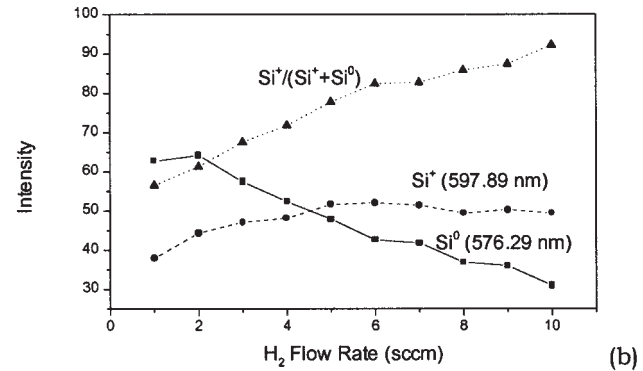


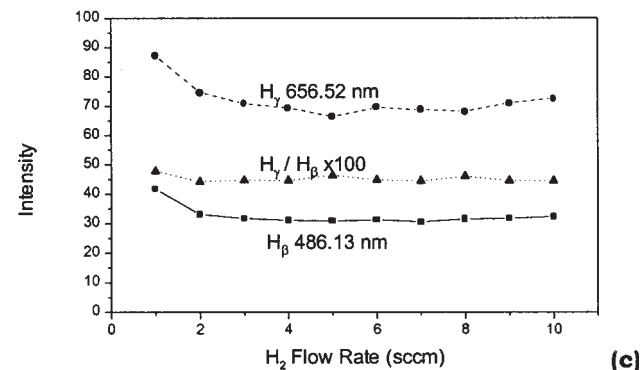
FIG. 7. Optical emission spectra show sputtered Si atom is ionized and hydrogen atoms are present in the ICP volume.



(a)



(b)



(c)

FIG. 8. Optical emission intensity shows that Ar ionization is reduced as the amount of hydrogen addition in (a), but the ionization ratio of sputtered Si is steadily increasing as in (b). H_β/H_γ remains constant while each intensity decreases in (c).

be calculated as $I_c/(I_c + yI_a)$; $y = 0.9$. The resultant fractions are shown in Table I. Our samples have crystalline fractions between 0.58 and 0.77. Other deposition conditions were chosen from our previous experiences on this experimental system: plasma diagnostics, tuning network modification, ICP frequency effect, and sputtering power to ICP power ratio.⁸⁻¹⁰ The positions of the crystalline peaks range from 508.3 to 517.8 cm^{-1} whereas the Si wafer has a main peak at 520.4 cm^{-1} in this experiment. The offset from the bulk Si peak would indicate the quality of crystallization of the film and the residual stress that is common in plasma-deposited films. This can be confirmed from the shift of the x-ray diffraction peak. The lattice parameter of standard sili-

con powder is $5.4309 \text{ \AA}$,¹¹ and calculated values of our current study range from 5.4668 to $5.4459 \text{ \AA}$. Based on this lattice spacing, I-PVD silicon films of this study have a tensile strain of about 0.66% – 0.28% . This can be a factor to shift the crystalline Raman peak as in Fig. 6.

D. Plasma diagnostics: Optical emission spectroscopic measurements

In I-PVD, gas pressure should be high enough to effectively thermalize and ionize fast-sputtered neutrals. Once ionized, the kinetic energy can be controlled by appropriate substrate bias. Optical emission spectra can be a good qualitative measure in estimating the composition of volume plasma. In the wide-range spectrum of Fig. 7, Si^0 (576.29 nm), Si^+ (597.89 nm), Ar^0 (675.28 nm), Ar^+ (668.42 nm), and H_γ (656.52 nm) are detected. In other channels of an optical multichannel analyzer, H_α (434 nm), H_β (486 nm), and SiH^* (414 nm) lines are detected, as opposed to Bae *et al.*; they reported that in capacitively coupled rf plasma, H_α and H_β lines were not noticeable.¹² The tendency of emission intensities was followed as hydrogen partial pressure increases; the ratio of ionic silicon [$= \text{Si}^+ / (\text{Si}^+ + \text{Si}^0)$] increases steadily whereas the argon ionization ratio remains constant in Figs. 8(a) and 8(b). Among hydrogen derivatives, H was emitting the strongest line, and the ratio of H_β to H_γ decreased slightly and does not change much beyond 2 sccm of hydrogen mixing in argon [Fig. 8(c)]. In I-PVD, the main advantage is thought to be the ionization of depositing silicon flux and retarding the ionized fast-reflecting neutrals such as hydrogen atoms. This explains why the x-ray diffraction results are insensitive to substrate temperatures between 150 and 250°C .

E. Effects of magnetron discharge voltage

In most of the cases in this study, a continuous dc power source was used to sputter silicon in $\text{Ar} + \text{H}_2$. As a test, a bipolar pulse power supply (ENI, RPG-10™, 10 kW , 100 – 250 kHz) was used to maintain an equivalent film deposition rate as the dc power source, but at most it gave smaller x-ray diffraction peaks. Pulsing in the several hundreds of kHz range tends to modulate the ion kinetic energy by sheath oscillation and might alter incoming ions' energy toward

higher values. The discharge voltage was found to be a sensitive parameter in depositing crystalline silicon in I-PVD. From a series of experiments, samples with magnetron discharge voltage higher than 600 V did not show well-developed polycrystalline peaks in x-ray diffraction data. With a 6-mm -thick target, the discharge voltage at 400 W was about 754 V at the beginning. Eroding the sputtering target (so that the leakage magnetic flux over the racetrack in the target becomes strong) reduced the discharge voltage down to a final value of 378 V in the lifetime. This is closely related to the reflected fast neutrals (mainly consisting of H). In a future study, the effects of magnetic field configuration (field intensity, balanced, or unbalanced) should be addressed in detail.

IV. CONCLUSION

Polycrystalline-silicon film was successfully deposited by ionized magnetron sputtering in a mixed gas environment of Ar and H_2 at a substrate temperature as low as 250°C , where the crystalline fraction based on the Raman data was around 70% and the grain size was 500 – $700 \text{ \AA}$.

ACKNOWLEDGMENT

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