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Etch characteristics of silver by inductively coupled fluorine-based plasmas

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Abstract

In this study, thin films of Ag deposited onto glass substrates were etched using inductively coupled fluorine-based plasmas. The effects of various process conditions on the Ag etch characteristics were evaluated to ascertain whether it would be possible to etch patterned Ag films with high etch rates and smooth sidewalls free of involatile etch products. It was found that involatile etch products remained on the substrate when films were etched in CF_4-based gas mixtures possessing either O_2 or N_2 as an additive. However, when Ar was added to either NF_3 or CF_4, a residue-free etch was obtained provided the partial pressure of Ar was no less than 50%. It is proposed that the residue-free Ag etch mechanism involves the formation of silver fluoride, which is physically sputtered by Ar^+ ions. A Ag etch rate of 160 nm/min with a Ag to photoresist etch selectivity exceeding 1.1 was achieved with an inductive power of 1500 W, a d.c. bias voltage of -180 V and a chamber pressure of 0.8 Pa with 50–50 CF_4/Ar partial pressures obtained with 60 sccm CF_4/60 sccm Ar flows. In addition, these conditions produced smooth Ag sidewall etch profiles.
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1. Introduction

Silver (Ag) has been identified as a potential material for use in thin film transistor liquid crystal displays (TFT-LCD) because it has the lowest room temperature bulk resistivity among metals and also possesses a high reflectivity. At room temperature, the resistivity of Ag is 1.59 $\mu\Omega$ cm. By comparison, the resistivities for gate-line materials currently in use for TFT-LCD arrays are 2.67 $\mu\Omega$ cm for pure Al, 5.0–7.0 $\mu\Omega$ cm for Al-alloys and 2.0 $\mu\Omega$ cm for Cu [1]. In addition, the reflectance of Ag is approximately 10–15% higher than that of Al. Thus, Ag shows great potential for use in TFT-LCD applications, as well as in state-of-the art integrated circuit (IC) applications [2].

In order to use Ag in TFT-LCDs, the films have to be patterned into fine lines, having 30–60° tapered sidewall profiles to promote step coverage. The required

film thickness for the Ag layer is 200–300 nm, and the minimum Ag feature width is approximately 8 μm. An appropriate etching process is indispensable. Due to the reduction of critical line dimensions coming in the next generation of TFT-LCD devices, plasma etching is preferable over wet etch methods. However, the following three problems must be solved before plasma etching of Ag can be used in TFT-LCD processing : (1) removal of involatile etch products; (2) overcoming low etch rates; and (3) removal of etch products without roughening the surface. For example, in previous studies the etching of Ag films with an O_2 plasma exhibited slow etch rates and high post-etch surface roughness [3–5]. Etching in mixtures of halogen gases such as Cl_2 or CF_4 with O_2 has also been reported [6,7]. During the etching of Ag films using Cl_2/O_2 plasmas, a thick involatile Ag etch product identified as silver oxychloride remained on the surface. This etch product produced a significant volume change, which stressed the Ag layer. Similarly, the etching of Ag films in CF_4/O_2 plasmas produced involatile etch products that coated

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the Ag surface. In this case, the residue was identified as silver fluorides or silver oxyfluoride. It was found that the resist wet strip process removed the etch product from the Ag surface, but the sidewall profile was left highly roughened [8].

The aforementioned two-step process demonstrates the potential of using dry etch technology to pattern fine lines of Ag. However, this multi-step method would add undesirable complexity to the process flow as well as increase the processing cost. Moreover, the method itself is problematic in that it causes rough sidewall profiles. The goal of this study is to identify a means of improving the patterning of Ag films using dry etch techniques. Fluorine-containing gas mixtures based upon either NF_3 or CF_4 were used in an inductively coupled plasma system to develop a one-step, high etch rate process yielding Ag structures exhibiting smooth sidewall profiles and clean, residue free surfaces.

2. Experimental

The Ag etch behavior was characterized with a magnetically enhanced inductively coupled plasma (MEICP) system. The tool consisted of a five-turn Au-coated copper coil located on the top of the process chamber, separated from the plasma environment by a 1-cm thick quartz window. A 13.56 MHz r.f. power supply was connected to the coil to generate the inductively coupled plasmas. A separate 13.56 MHz r.f. power supply was attached to the 6-inch-diameter substrate electrode to provide a d.c. bias voltage to the sample. The distance between the quartz window and the substrate electrode was 7.5 cm. Substrates were placed atop the substrate electrode without clamping. Cooling was provided by chilled water, keeping the substrate temperature at or near room temperature. Four sets of permanent magnets, each possessing 2000 G, were installed around the chamber wall to increase plasma density and uniformity by confining the plasma. Details of this MEICP system are described elsewhere [9].

The samples consisted of 500-nm thick Ag films deposited on 10×10 cm LCD-grade glass substrates by r.f. sputtering. The Ag films were patterned with a 2.0-μm thick photoresist mask, possessing an 8.0 μm minimum feature size and a sidewall taper of approximately 30°. The fluorine-based gases, CF_4 and NF_3, were used as the main etch gases, while Ar, O_2 and N_2 were used as additive gases. It was not possible to employ automatic pressure control in this study because the exhaust port of the etch tool was configured with a manually operated throttle valve. In order to control the chamber pressure, the throttle valve was left fully open. The desired total pressure was then acquired by sequentially adjusting the flow of each gas component into the etch chamber to achieve a desired partial pressure value by using mass flow controllers (MFCs). These adjust-
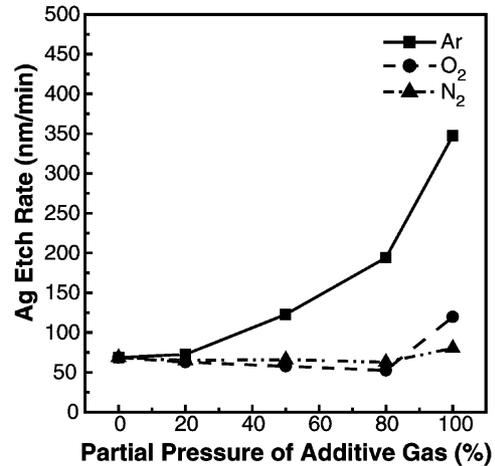

Fig. 1. Ag etch rate as a function of the additive gas partial pressure for CF_4/Ar, CF_4/O_2 and CF_4/N_2 gas mixtures using an inductive power of 1500 W, a d.c. bias voltage of -150 V, and a chamber pressure of 0.8 Pa. The horizontal axis units in this figure are expressed as a percentage of the total chamber pressure.

ments were made prior to striking a plasma. Upon striking a plasma, the chamber pressure typically rose by approximately 15%. No effect was made to compensate for this increase. The range of the key plasma parameters investigated in this study were: (1) 300–1500 W for the inductive power; (2) 0 to -180 V for the d.c. bias; and (3) 0.4–2.7 Pa for the chamber pressure, which required us to vary the total gas flow from approximately 25 to 160 sccm.

The Ag etch rate was determined using stylus profilometry of the feature depth after stripping the photoresist. A scanning electron microscope (Hitachi, S-2150 SEM) was used to observe the as-etched Ag surfaces. The characteristics of the fluorine-based plasmas during the Ag etching were measured by optical emission spectroscopy (SC Technology, PCM402). Composition of the etch by-product deposited on the quartz window located at the top of the process chamber was analyzed by Auger electron spectroscopy (PHI-670).

3. Results and discussion

Fig. 1 shows how the etch rate of Ag responds to the addition of either O_2, N_2 or Ar to CF_4. An inductive power of 1500 W, a d.c. bias of -150 V and a chamber pressure of 0.8 Pa were used to etch the Ag. Due to the formation of low volatility etch products for the CF_4/O_2 and CF_4/N_2 gas mixtures, the etch rates of Ag were estimated after removing the photoresist in a stripper solution because the stripper also removed the etch products from the substrate. As shown in the figure, the addition of O_2 or N_2 to CF_4 had a nearly benign affect on the Ag etch rate. However, when Ar was added to
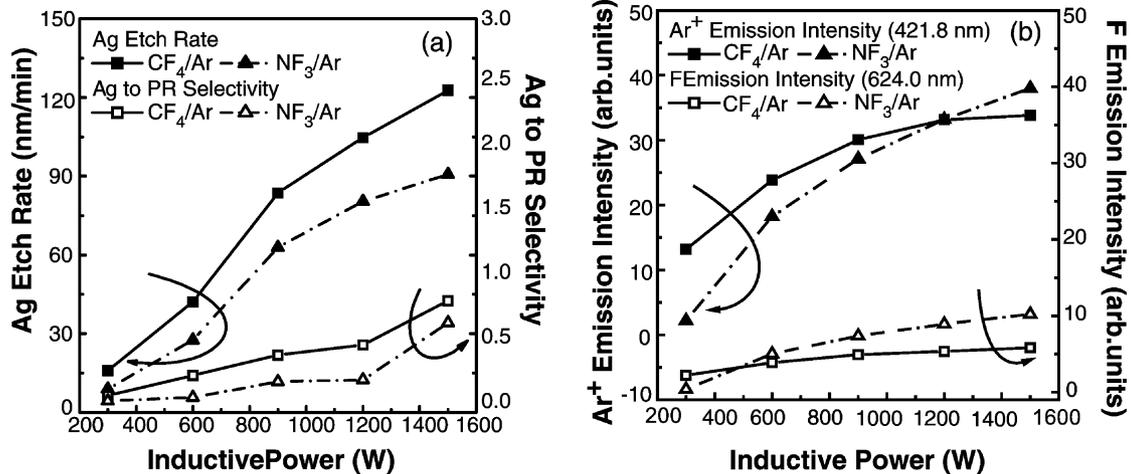
Fig. 2. Response of (a) Ag etch rates and Ag to PR etch selectivity and (b) OES of F and Ar$^+$ emission lines as a function of inductive power using a d.c. bias voltage of -150 V and a chamber pressure of 0.8 Pa.

CF$_4$ the Ag etch rate was found to increase as a function of increasing the percentage of Ar in the gas mixture.

It is believed that the addition of O$_2$ to CF$_4$ produces etch by-products consisting of silver fluoride, silver oxyfluoride and silver oxide. Each of these compounds have low volatilities and tend to form dense overlayers on the surface of the Ag films during the etch process. Similar behavior appears to occur for the etch by-products associated with N$_2$ addition to CF$_4$. As shown in Fig. 1, the creation of these film layers has a benign affect on the Ag etch rate. However, for the case of Ar addition to CF$_4$, the low volatility silver fluoride formed by CF$_4$ appears to be readily etched via sputtering by Ar$^+$ ions. Such behavior is consistent with a chemically-assisted physical sputtering etch mechanism. It should be noted that the largest Ag etch rate was obtained when pure Ar was used. A previous investigation found that the sputter yield of Ag exposed to 400 eV Ar$^+$ ions was 3.4 atoms/ion [10]. Unfortunately, the use of pure Ar to etch Ag is not practical in an inductively coupled plasma system. The reasons being that: (1) a conductive Ag film layer is deposited onto the dielectric quartz window, which blocks the r.f. power transmission to the plasmas; and (2) an insoluble Ag residue forms on the sidewall of the etched Ag structures. In conclusion, there are two advantages of mixing Ar with CF$_4$. First, only non-conductive compounds form on the dielectric window, so the transmission of r.f. power into the plasma is not impeded. Second, when Ar is added to CF$_4$ in a concentration equal to or greater than 50%, the etched Ag films are free of any etch residue. We wish to note that in a separate study we found that chlorine-based plasmas are not amenable to removing etch residues such as silver chloride [11]. Therefore, in this study, it was decided to explore the effect of varying other etch parameters such as r.f. power, bias voltage and chamber

pressure, using 50–50 partial pressures of either CF$_4$/Ar or NF$_3$/Ar in the gas mixture, in order to investigate the mechanism of in-situ removal of the etch products. The corresponding gas flow ratios for the above CF$_4$/Ar and NF$_3$/Ar partial pressure conditions are approximately 60 sccm CF$_4$/60 sccm Ar and 70 sccm NF$_3$/60 sccm Ar, respectively, at 2 Pa of total pressure.

Fig. 2 shows the effect of varying the inductive power on: (a) the Ag etch rate and the Ag to photoresist (PR) etch selectivity; and (b) the optical emission intensities from Ar$^+$ ions and F radicals for CF$_4$/Ar and NF$_3$/Ar gas mixtures. For the sake of consistency, all optical emission spectroscopy data presented in this work compares the 624.0 nm F radical peak to the 421.8 nm Ar$^+$ ion peak. Also, as concerns Fig. 2b the d.c. bias voltage was maintained at -150 V and the operating pressure at 0.8 Pa. Fig. 2a shows that an increase in the inductive power increased both the Ag etch rate and the Ag to PR etch selectivity. Also, as shown in Fig. 2b, the increase of inductive power increased optical emission intensities from the Ar$^+$ ions and the F radicals.

Fig. 3 shows the effect of varying the d.c. bias voltage (0 to -180 V) on: (a) the Ag etch rate and the Ag to PR etch selectivity; and (b) the optical emission intensity response from Ar$^+$ ions and F radicals for CF$_4$/Ar and NF$_3$/Ar gas mixtures. An inductive power of 1500 W and an operating pressure of 0.8 Pa were used for these measurements. Fig. 3a shows that an increase in d.c. bias voltage increases both the Ag etch rate and the Ag to PR etch selectivity. A maximum Ag etch rate of 160 nm/min with a Ag to PR etch selectivity exceeding 1.1 was achieved with an inductive power of 1500 W, a d.c. bias voltage of -180 V and an operating pressure of 0.8 Pa for the CF$_4$/Ar gas mixture. The F radical and Ar$^+$ ion optical emission intensities for the CF$_4$/Ar gas mixture, shown in Fig. 3b, were unresponsive to the
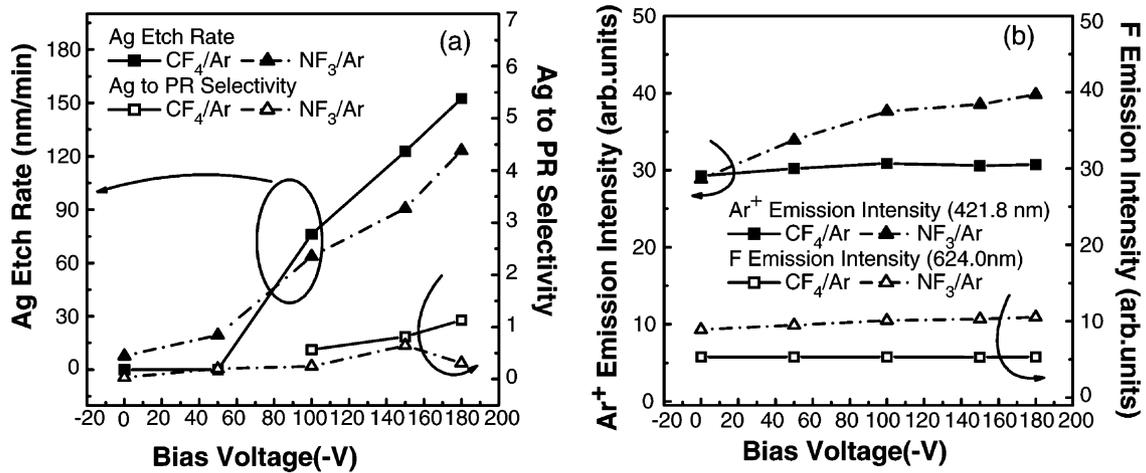
Fig. 3. Response of (a) Ag etch rates and Ag to PR etch selectivity and (b) OES of F and Ar$^+$ emission lines as a function of bias voltage using an inductive power of 1500 W and a chamber pressure of 0.8 Pa.

increase of d.c. bias voltage. This result suggests that there is no significant change of F radical density and Ar$^+$ ion density as a function of the d.c. bias voltage. Therefore, it is likely that the increases in the Ag etch rate and the Ag to PR etch selectivity are produced by an increase in the silver fluoride sputter yield due to the increase of the Ar$^+$ ion energy bombarding the surface [12,13].

Fig. 4 shows the effect of varying the chamber pressure (0.4–2.7 Pa) on: (a) the Ag etch rate and the Ag to PR etch selectivity; and (b) the optical emission intensity response from Ar$^+$ ions and F radicals for CF$_4$/Ar and NF$_3$/Ar gas mixtures. The inductive power was kept at 1500 W and the d.c. bias voltage at -150 V for these measurements. As shown in Fig. 4a, an increase in chamber pressure tended to decrease both the Ag etch rate and the etch selectivity. Optical emis-

sion intensities from Ar$^+$ ions and F radicals, shown in Fig. 4b, increased with the increase in chamber pressure. This response suggests that both the Ar$^+$ ion density and F radical density increased monotonically with chamber pressure. We believe that an increase in chamber pressure may cause a decrease in the Ar$^+$ ion energy as the result of multiple scattering of ions as they cross the plasma sheath to the Ag surface. This decrease in ion energy will result in a decrease in the sputter yield for both Ag and silver fluoride, resulting in a net decrease in the Ag etch rate. In conclusion, Figs. 2–4 support the assertion that the variation of Ag etch rate and Ag to PR etch selectivity with inductive power, d.c. bias voltage and chamber pressure can be explained by the interplay between the formation of silver fluoride by F radicals and the removal of silver fluoride by energetic Ar$^+$ ions.
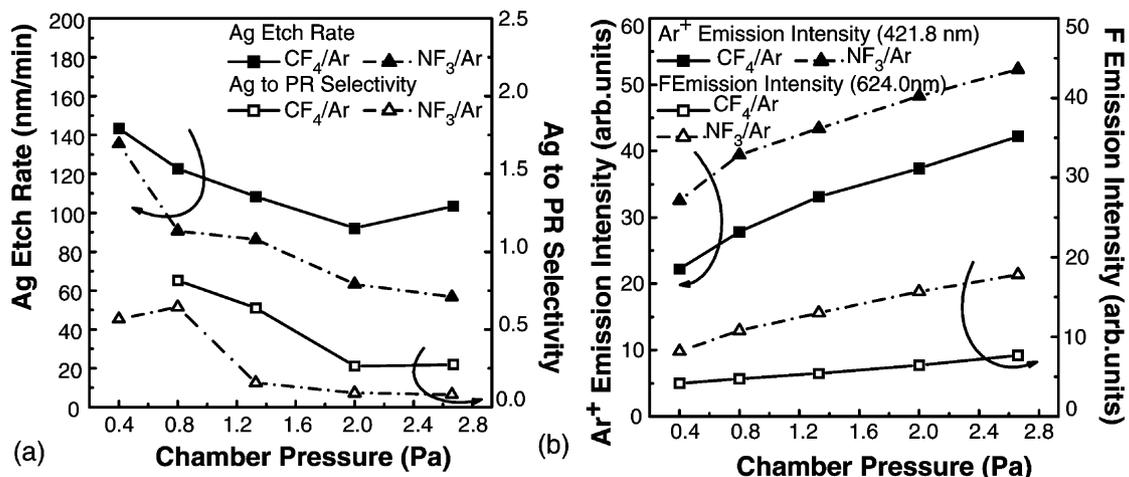

Fig. 4. Response of (a) Ag etch rates and Ag to PR etch selectivity and (b) OES of F and Ar$^+$ emission lines as a function of chamber pressure using an inductive power of 1500 W and a d.c. bias voltage of -150 V.
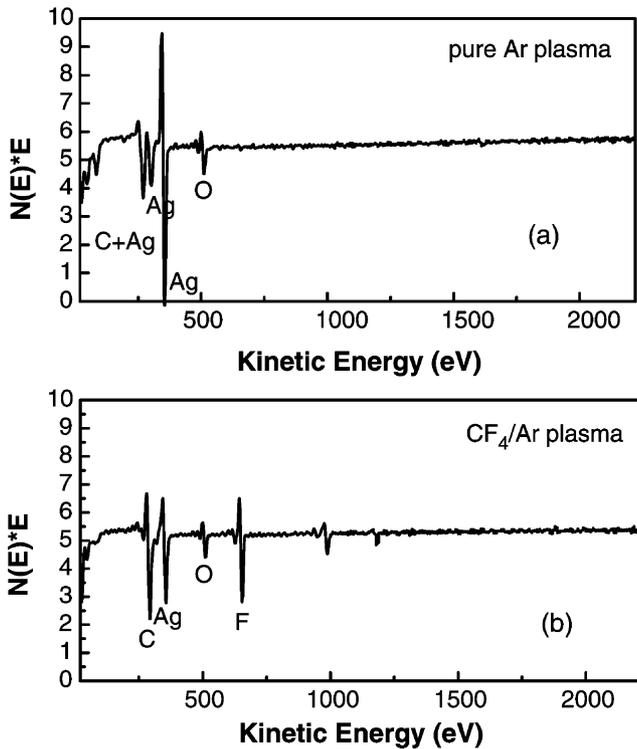
Fig. 5. AES data identifying the composition of the film layer that forms on the dielectric window by (a) pure Ar sputtering and (b) a 50–50 partial pressures of CF_4/Ar using an inductive power of 1500 W, a d.c. bias voltage of −150 V and a chamber pressure of 0.8 Pa.

Fig. 5 presents Auger electron spectroscopy (AES) measurements, which identify the composition of the film layer that forms on the dielectric quartz window at the top of the process chamber during the Ag etch process. As already noted, our empirical observations found that fluorine-based gases mixed with Ar produce a non-conducting silver fluoride layer on the dielectric window as opposed to a conducting Ag layer that forms when pure Ar is used. Samples for these measurements were obtained by affixing a small silicon wafer onto the dielectric window to collect film material during the Ag etch process. Fig. 5 contrasts the composition of films produced by a pure Ar plasma versus a CF_4/Ar gas mixture. The spectra in the figure show that the use of pure Ar produced a film on the Si wafer exhibiting a strong signal for Ag. Conversely, for the case of the CF_4/Ar gas mixtures, comparable signal levels of F, Ag and C were detected. This latter result is consistent with our assertion that silver fluoride forms on the dielectric window. In point of fact, when pure Ar was used to etch Ag, a coating of conductive Ag formed on the dielectric window within a few minutes, preventing the transmission of inductive r.f. power to the plasma. However, when a CF_4/Ar gas mixture was used, a yellowish material related to silver fluoride (AgF: yellow, AgF_2: white or brown) [14] coated the entire

chamber, including the dielectric window. In this latter case, the film layer did not inhibit the operation of the inductive plasma. Moreover, the deposited material was easily removed using wipes soaked in alcohol.

Fig. 6 shows SEM micrographs of a Ag film etched in a CF_4/Ar plasma. No etch by-product such as silver fluoride is present upon completing the etch (Fig. 6a). In addition, the sidewalls of the Ag etch profile were observed to be smooth after the photoresist was stripped off (Fig. 6b).

4. Conclusions

In this study, CF_4 and NF_3 fluorine-based gas mixtures were used in an inductively coupled plasma system to investigate the possibility of etching Ag in a single-step high etch rate process , producing structures with smooth sidewall profiles that are free of low volatility etch by-products. Also, the characteristics of the plasmas and the Ag etch response were investigated as a function of inductive power, bias voltage and chamber pressure to gain an understanding of the Ag etch mechanism.

It was found that Ar addition to either NF_3 or CF_4 with a partial pressure equal to or exceeding 50%
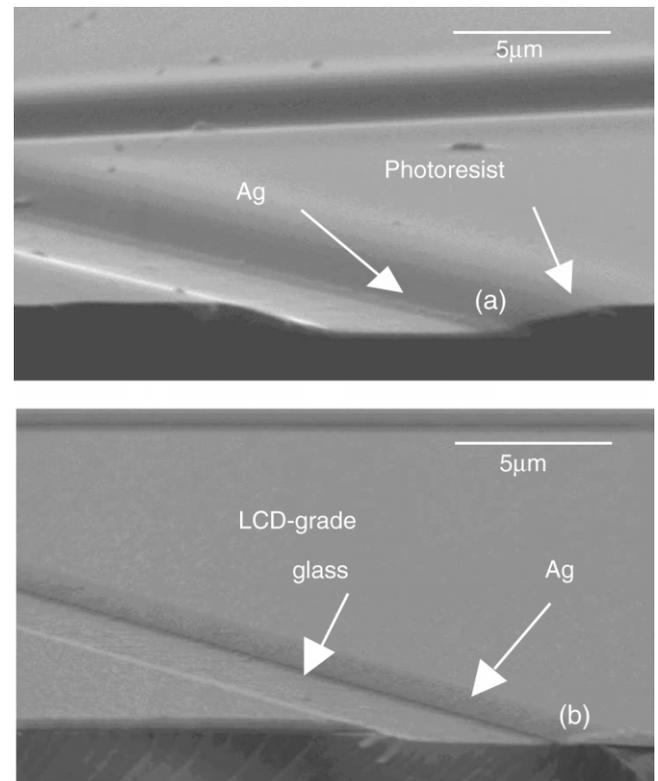

Fig. 6. SEM micrographs of (a) an etched Ag film with the photoresist pattern still in place and (b) etched Ag film after stripping off the photoresist. The plasma conditions for etching this film were a 50–50 partial pressure of CF_4/Ar with an inductive power of 1500 W, a d.c. bias voltage of −150 V and a chamber pressure of 0.8 Pa.

yielded residue-free Ag etching. The response of the Ag etch rate and the Ag to PR selectivity to inductive power, d.c. bias voltage and chamber pressure is consistent with a chemically-assisted physical sputtering etch mechanism. Therefore, it is concluded that residue-free, high rate Ag etching in fluorine-based mixtures, for a partial pressure of Ar that is no less than 50%, proceeds by the formation of low volatility silver fluoride by F radicals, which is simultaneously removed by Ar^+ ion sputtering. The optimized process etched Ag at a rate of 160 nm/min with a Ag to PR etch selectivity exceeding 1.1. The plasma conditions yielding this result were an inductive power of 1500 W, a d.c. bias voltage of -180 V and a chamber pressure of 0.8 Pa with 50–50 CF_4/Ar partial pressures. In addition to providing a high etch rate, these conditions also produced etch structures exhibiting smooth sidewalls.

Acknowledgments

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