Crystallization transformations in vacuum-deposited amorphous aluminum fluoride self-developing thin-film resists induced by electron-beam irradiation

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Conventional transmission electron microscopy is employed to investigate in situ electron-beam-induced phase transformations in vacuum-deposited amorphous aluminum fluoride (a-AlF3) self-developing thin-film resists. The a-AlF3 resists exhibit a very complex sequence of crystallization transitions with three crystalline materials (Al, AlF3, and Al2O3) formed sequentially as the electron dose increases from 10^5 to 10^7 Cm^{-2}. Thermally evaporated “dry” a-AlF3 is dissociated into Al crystalline colloids at a threshold dose of ~1x10^5 Cm^{-2}, and begins to transform into crystalline AlF3 (c-AlF3) at a dose of ~1x10^6 Cm^{-2}. However, water contained in the “wet” films accelerates the transition of a-AlF3 to c-AlF3 at a reduced threshold dose of ~2x10^5 Cm^{-2}. Moreover, a-AlF3 films prepared by electron-beam deposition require a markedly different dose for each substance to crystallize, attributed to a microstructure variation. For all of the a-AlF3 films, textured Al2O3 is formed at doses of ~1x10^7 Cm^{-2}, also with the aid of H2O absorbed from the microscope vacuum and by the following chemical reaction: 2AlF3(s) + 3H2O(g) → Al2O3(s) + 6HF(g). © 2002 American Vacuum Society. [DOI: 10.1116/1.1464842]

I. INTRODUCTION

Vacuum-deposited amorphous AlF3 (a-AlF3) thin films have been used by several research groups to fabricate nanostructures. Under the impingement of a finely focused electron beam of current densities typically 10^5–10^7 A m^{-2}, the exposed site can be self-developed, subsequently forming a variety of nanometer-sized features (such as holes and trenches) of sizes less than 5 nm. Previous investigations usually assumed that the self-developing behavior of a-AlF3 thin-film resists was unaffected by the films’ humidity or environmental factors. However, evaporated a-AlF3 thin films are normally porous and thus easily absorb varying amounts of water, some of which is chemically bonded to AlF3 and some of which is physisorbed on the surface and in the pores. We have previously demonstrated that thermally evaporated a-AlF3 thin films undergo a sequence of phase-transition processes, which are highly sensitive to the presence of water, if damaged using a broad beam of electrons in a transmission electron microscope (TEM). In this article the electron-beam-induced phase-transition behavior of thermally evaporated and electron-beam (e-beam) deposited a-AlF3 thin-film resists is further investigated. Factors influencing the transformation of the new crystalline phases (Al, AlF3, and Al2O3) and the self-developing behavior of vacuum-deposited AlF3 resists are also discussed.

II. EXPERIMENTAL PROCEDURES

All of the a-AlF3 thin films were deposited by an Edwards Auto 306 vacuum coater. Three types of sample films were examined: thermally evaporated “dry” films, thermally evaporated “wet” films, and e-beam deposited “dry” films, all three being coated directly on self-supporting amorphous carbon films (5 nm thick) on 3 mm copper grids. The thicknesses of the films, as measured with a quartz crystal monitor, were all ~50 nm (~2%). For the thermally evaporated and e-beam deposited dry films, anhydrous AlF3 powder was dehydrated at 400 °C for 10 h to remove the absorbed water completely prior to evaporation. For the wet films, AlF3 • 3H2O powder was evaporated thermally without preheating. The two (thermal and e-beam) dry films were deposited at a lower pressure of around 5x10^{-4} Pa (~4x10^{-6} Torr), whereas the wet a-AlF3 films were thermally evaporated at a markedly higher pressure of ~10^{-2} Pa. Such an enormous increase in the background pressure is due to the release of H2O from the hydrated AlF3 • 3H2O. The amount of H2O absorbed to the AlF3 films was examined using Fourier transform infrared spectroscopy (FTIR) to identify the O–H absorption band at 3300 cm^{-1}.

All films were freshly prepared and transferred to a JEOL 2000FX transmission electron microscope within 15 min of preparation. Beam-irradiation experiments were carried out in situ with the microscope operating at an acceleration voltage of 100 kV in conjunction with a Gatan parallel electron energy loss spectrometer (EELS). The beam current was...

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measured using a Faraday cage at the side of the specimen, which was set at 31.1 nA and routinely checked every 10 min, making sure that any decay of the beam current was compensated for. The condenser lens C2 was overfocused to give a uniform irradiation area of $4.5 \times 10^{-12}$ m$^2$ (or $8.0 \times 10^{-12}$ m$^2$). This adjustment led to damage of the films by a probe of current density $6.9 \times 10^3$ A m$^{-2}$ (or $3.9 \times 10^3$ A m$^{-2}$). The same area of the specimen was irradiated throughout each experiment, with the irradiation being stopped at frequent intervals for a series of selected area diffraction patterns to be obtained. These selected area diffraction patterns were all obtained under identical exposure and plate-developing conditions, thereby facilitating direct comparisons of all the patterns by measuring the intensities of the diffraction rings.

III. RESULTS AND DISCUSSION

Four diffraction patterns from a prolonged damage series of a thermally evaporated dry AlF$_3$ film are shown in Figs. 1(a)–1(d). It can be seen from this set of figures that the as-deposited amorphous AlF$_3$ film originally contains only diffuse rings [Fig. 1(a)], and begins yielding sharp diffraction rings of Al and crystalline AlF$_3$ ($c$-AlF$_3$) at doses of $\sim 1 \times 10^5$ and $\sim 1 \times 10^6$ Cm$^{-2}$, respectively [Figs. 1(b) and 1(c)]. After prolonged irradiation with a dose of $1 \times 10^7$ Cm$^{-2}$, a strong 0.14-nm Al$_2$O$_3$ diffraction ring emerges [Fig. 1(d)]. It is interesting to note that tilting the specimen did not reveal any visible change in the intensities of Al and AlF$_3$ rings. However, when adequately titled, the 0.14-nm Al$_2$O$_3$ diffraction ring changed to two arcs, along with the appearance of four arcs centered at 0.197 nm. This finding indicates that the Al$_2$O$_3$ crystals possess a textured structure.

Dark field images, carefully recorded from $a$-AlF$_3$ films by placing an objective aperture on diffuse rings of Fig. 1(a), exhibit a speckle contrast also reminiscent of an amorphous structure [see Fig. 2(a)]. As evidenced from the Al (1 1 1) dark field image in Fig. 2(b), an electron dose of $\sim 1 \times 10^5$ (or 2 $\times 10^5$) Cm$^{-2}$ has already produced many Al equiaxed crystallites of sizes $\leq 10$ nm. Gradually increasing the dosage caused the Al crystallites to grow equatorially. Ultimately, at doses of $\geq 1 \times 10^6$ Cm$^{-2}$, crystalline Al colloids of sizes from 5 to 30 nm were observed. Dark field images recorded from AlF$_3$ (1 1 0) reveal that a dose of $\geq 1 \times 10^6$ Cm$^{-2}$ is required to produce a significant amount of AlF$_3$ nanocrystallites [see Fig. 2(c)]. Al$_2$O$_3$ textured crystallites, which distribute evenly throughout the matrix, can be observed only at a substantially high electron dose of $1 \times 10^7$ Cm$^{-2}$ or greater. [Fig. 2(d)]. Recording a highly magnified dark field image such as that depicted in Fig. 2 requires a dose of at least $5 \times 10^4$ Cm$^{-2}$. Therefore characterizing the phase-transition behavior of the $a$-AlF$_3$ films simply by using TEM imaging is difficult because the dosage needed to record a micrograph inevitably damages the films seriously. Conversely, the dosage received by a film during the recording of a selected area electron diffraction pattern can be optimized to only $3 \times 10^5$ Cm$^{-2}$. Thus electron diffraction analysis was hereinafter conducted to further elucidate the phase-transition process.

The diffraction technique was performed by irradiating the same area of each film, during which the irradiation was stopped at frequent intervals for a series of selected area diffraction patterns to be recorded (for details see Sec. II). Each set of patterns was individually digitized and radially averaged to produce intensity as a function of scattering angle (2$\theta$). Figure 3 shows the resultant diffraction intensities at four dosages for thermally evaporated dry AlF$_3$ films damaged at a current density of $6.9 \times 10^3$ A m$^{-2}$, illustrating that the damage process proceeds with the broad peaks of $a$-AlF$_3$ disappearing and sharp peaks of the crystalline substances (Al, AlF$_3$, and Al$_2$O$_3$) appearing. (It is to be noted that the results presented herein are also typical of current density at $3.9 \times 10^3$ A m$^{-2}$.) Because each plate was recorded and developed under identical conditions, the beam-induced phase-transition behavior can be assessed by directly comparing the intensities of the diffraction rings. For each of the three specimens (the thermally evaporated dry and wet films and e-beam deposited dry film), diffraction patterns were obtained as in Fig. 1 over a range of doses from $10^5$ to $10^6$ Cm$^{-2}$, radially averaged as in Fig. 3 and the areas under
the most prominent peak for each crystalline product found. These diffraction peak areas are plotted as a function of dosage in Figs. 4~a!–4~c!, allowing the phase transformations to be compared quantitatively.

Comparing Figs. 4~a! and 4~b! reveals that, for the dry and wet thermally evaporated films, the progress of aluminum crystallization is similar, with aluminum forming at a slightly lower dose (~1 × 10⁵ Cm⁻²) in the dry film and the maximum intensity being higher by ~50%. The amount of Al for both films levels off above a dose of 1 × 10⁶ Cm⁻². However, a much lower dose (~2 × 10⁵ Cm⁻²) is needed for the a-AlF₃ to crystallize in the wet film than in the dry film (~1 × 10⁶ Cm⁻²). In addition, if the dry film is exposed to air for a few days then the behavior of forming c-AlF₃ becomes more akin to that of the wet film. Although the wet film examined here was unusual in this respect, Fourier transform infrared spectroscopy showed that this film indeed exhibited an enormous O–H absorption band, whereas the O–H absorption band was absent from the dry film.⁸ This finding indicates that water accelerates the crystallization transition of a-AlF₃, forming c-AlF₃. It is to be noted that a-AlF₃ resists of a limited thickness range (40–120 nm) are damaged in parallel throughout the irradiated volume of the sample film.¹⁰ Thus the amounts of aluminum and c-AlF₃ crystallites produced within the beam/sample interaction volume (beam-volume) are expected to scale with the thickness of the sample films. As the films examined herein all have a thickness of 50 nm ± 2%, the differences in amounts of aluminum (or c-AlF₃) in Fig. 4 are mainly related to differences in intrinsic properties of the samples.

As Figs. 4(a) and 4(c) show, the main difference between the thermally and e-beam evaporated dry AlF₃ films is that much less aluminum is formed in the e-beam evaporated film over the whole range of dosages, while the crystallization of a-AlF₃ in this film behaves in a fashion similar to that of the thermal film, but with ~1.8 times as much c-AlF₃. For the e-beam film, diffraction peaks of Al in the original patterns (TEM micrographs) were rather weak over the whole range of doses from 10⁵ to 10⁷ Cm⁻². This observation suggests
that although the water content in the dry thermal and dry e-beam films is similar and low, there is an additional structural difference between films produced by the two deposition methods. Thermally evaporated AlF\textsubscript{3} films are deposited by using thermal energy alone for driving evaporation, reaction, and film structure development, while electron-beam deposited films are produced by using an energy beam ~5 kW! to vaporize the AlF\textsubscript{3} source and to activate the surface mobility of adatoms. Thus electron-beam deposited films are normally denser than thermally evaporated films. Moreover, aluminum colloids are formed primarily by radiolytic decomposition of AlF\textsubscript{3} instead of beam-heating effects.\textsuperscript{11} The film’s microstructure (e.g., porosity) thus could be an important factor deciding the efficiency of radiolysis. As having a greater degree of porosity, the thermally evaporated films would contain a higher initial concentration of intrinsic defects, allowing radiolysis to occur easier as more interstitial/substitutional sites are available to accommodate the beam-induced defects. Indeed, in situ observation during damaging of the sample films with a broad beam in a TEM (or rastering by a focused probe in a dedicated scanning transmission electron microscope) revealed that irradiated volumes of thermally evaporated films lose their integrity within a short period of ~3 s or less, whereas those of e-beam deposited AlF\textsubscript{3} films can maintain their morphology for tens of seconds.

For a dry thermal \( a \)-AlF\textsubscript{3} film, measurements were made of the areas under the oxygen and fluorine K edges of EELS spectra as a function of dosage (Fig. 5). During these EELS measurements, the beam current was kept constant and the same area irradiated. It can be seen from Fig. 5 that, up to a dose of \( 1 \times 10\textsuperscript{6} \text{ Cm}\textsuperscript{-2} \), fluorine decreases rapidly, then more slowly and at a uniform rate above this dose. \( 1 \times 10\textsuperscript{6} \text{ Cm}\textsuperscript{-2} \) corresponds to the dose when \( a \)-AlF\textsubscript{3} starts to crystallize. Thus up to \( 1 \times 10\textsuperscript{6} \text{ Cm}\textsuperscript{-2} \), fluorine is being lost and the AlF\textsubscript{3} remains amorphous. AlF\textsubscript{3} begins to crystallize at \( 1 \times 10\textsuperscript{6} \text{ Cm}\textsuperscript{-2} \) and is more stable to damage. Therefore the rate of loss of fluorine decreases, corresponding to the flat of Al intensities at this dose (see Fig. 4). Our previous study\textsuperscript{10} found that the doses required for AlF\textsubscript{3} resists to develop fully are on the order of \( 10\textsuperscript{5} \text{ Cm}\textsuperscript{-2} \). This order of doses is also required for \( a \)-AlF\textsubscript{3} to transform into Al and \( c \)-AlF\textsubscript{3}. As \( c \)-AlF\textsubscript{3} is less sensitive to radiolysis than \( a \)-AlF\textsubscript{3}, the efficiency of developing \( a \)-AlF\textsubscript{3} resists will be retarded by the amorphous-to-crystalline transformation of AlF\textsubscript{3} found in this work.

The formation of the textured Al\textsubscript{2}O\textsubscript{3} in all three films at the high-dose regime (~\( 1 \times 10\textsuperscript{7} \text{ Cm}\textsuperscript{-2} \)) is interesting. According to Fig. 5, the oxygen 535-eV edge is present in lightly damaged films (~\( 2 \times 10\textsuperscript{5} \text{ Cm}\textsuperscript{-2} \)), but no crystalline Al\textsubscript{2}O\textsubscript{3} is seen in Fig. 4. The oxygen, presumably in the form of H\textsubscript{2}O picked up from the microscope vacuum, is gradually incorporated into the AlF\textsubscript{3} film as the fluorine is lost. Above \( 1 \times 10\textsuperscript{7} \text{ Cm}\textsuperscript{-2} \), textured Al\textsubscript{2}O\textsubscript{3} begins to form suddenly, corresponding to a sharp decrease in the amount of \( c \)-AlF\textsubscript{3} and an abrupt increase in the oxygen concentration at this dose (compare Figs. 4 and 5). This finding suggests that the textured Al\textsubscript{2}O\textsubscript{3} is formed by a reaction between AlF\textsubscript{3} and H\textsubscript{2}O. Thus the following chemical reaction equation is proposed:
\[ 2\text{AlF}_3(s) + 3\text{H}_2\text{O}(g) \rightarrow \text{Al}_2\text{O}_3(s) + 6\text{HF}(g) \]. As the dose exceeds \(5 \times 10^7 \text{ Cm}^{-2}\), the concentration of oxygen levels off when all the AlF\(_3\) has reacted, and Al\(_2\)O\(_3\) may itself be decomposing due to irradiation.\(^{12}\)

### IV. CONCLUSION

We have shown that the electron-beam damage of self-developing \(\alpha\)-AlF\(_3\) thin-film resists is a very complex process whereby crystalline aluminum is formed first at doses of \(\geq 1 \times 10^5 \text{ Cm}^{-2}\) as fluorine is lost, followed by the crystallization of the \(\alpha\)-AlF\(_3\) into \(\text{c-AlF}_3\) normally at \(1 \times 10^6 \text{ Cm}^{-2}\). At doses of \(\geq 1 \times 10^7 \text{ Cm}^{-2}\), the oxygen (presumably due to water) in the microscope ambient reacts with the AlF\(_3\) to form textured Al\(_2\)O\(_3\). It is important to note that both the water content of the films and the deposition method can greatly alter the dosage required for each crystalline substance to form. The alternation of the phase transitions by these factors has implications for nanofabrication of self-developing inorganic electron-beam resists.

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