Spectroscopic Investigation of AgO_x Films for Super Resolution Near Field Structure Application

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Abstract—In this work thin silver oxide layers (AgO_x) were prepared by reactive sputtering of a silver target in oxygen containing atmosphere. We report a gradual composition change of the deposited layers with increasing oxygen concentration from Ag over Ag_2O to AgO and furthermore that dispersed silver clusters are present even up to high O_2 concentrations. Raman- along with IR-spectroscopy and ellipsometric measurements reveal specified compounds at defined oxygen concentrations. Optical transmission and reflection measurements as a function of temperature show that these compounds exhibit phase transitions (i.e. AgO decomposes to Ag_2O and finally to Ag), connected to considerable refractive index changes. This work was done with respect to super-Resolution Near-Field Structures where these effects are exploited to realize ultra high optical data storage in combination with magneto-optical and phase change recording materials.

Key words: silver oxide, reactive sputtering, micro Raman spectroscopy, super-RENS optical data storage

1. Introduction

Interactions between silver and oxygen have been described in several papers¹⁻²⁾. The general outcome is that the silver oxide chemistry is very complex due to multiple charge states in which the Ag-ion can exist despite its low oxidation potential. Silver oxide compounds are therefore relatively unstable and show a noticeable tendency to decompose into the elements at elevated temperatures. Furthermore the composition and stability of silver oxides depend strongly on the preparation method (chemically, electrochemically or sputtered) and hence the published data for properties scatter over a wide range like for example the decomposition temperature of Ag_2O with values in between 160 °C to 430 °C.

To our knowledge few information on the composition and optical properties of reactively sputtered AgO_x layers is reported in the literature. Nevertheless such layers play an important role for Light Scattering

Center super-REsolution Near-Field Structure (Isc-super-RENS) optical data storage³⁾. Kim et al. showed recently⁴⁾ that the application of a sputtered AgO_x layer in combination with a conventional magneto-optical storage layer enables the generation of marks with dimensions well below the diffraction limit at high carrier to noise ratios. This technique neither needs any near field optics nor elaborate controlling mechanisms and is therefore considered to be a promising technique for future ultra high density optical data storage. The mask layer mechanism is thought to be based on the reversible thermal decomposition of the AgO_x to Ag and O_2 in a laterally confined region. The Ag clusters work as a near field scattering center and produce an optical high intensity near field to write and read out marks with sub wavelength dimensions in an adjacent recording layer. However the mechanism is not fully understood yet and the intention of this work is to determine the chemical and optical characteristics of the sputtered AgO_x mask layers.

For this purpose silver oxide layers were deposited by sputtering with resembling parameters to that of the super-RENS disk fabrication. The oxygen concentration in the sputtering gas mixture was varied from 0 to 100% to obtain layers of different composition. These layers were probed by Raman- and IR-spectroscopy and the complex refractive indices were measured by ellipsometry. The thermal behavior i.e. the decomposition of the deposited compounds, was observed by optical transmission measurements on a micro heating stage. Furthermore, silver oxide layers were sputtered on polycarbonate disks and sandwiched with $\text{ZnS-SiO}_2\text{-CeO}_2$ to imitate super-RENS conditions. Such disks were probed dynamically by means of an optical disk drive tester.

2. Experimental

Silver oxide films were deposited by reactive r.f. magnetron sputtering at room temperature with a 3-inch Ag target (99.99% purity) on either slide glass, polished silicon wafers or polycarbonate disks at a target to substrate distance of 40 mm. The sputtering system was a Shibaura Mechatronics CFS-4ES with

a rotary/turbo molecular pump configuration. Films of different composition were deposited by changing the gas ratio of O₂ and Ar under a background pressure of less than 6×10^{-4} Pa. Since the deposition rate changed with oxygen content, the sputtering time was always adjusted to obtain films of 300 nm thickness. The Ag target was pre-sputtered in the respective atmosphere for one minute. The sputtering pressure and applied r.f. power were fixed at 0.5 Pa and 200 W (4.4 W/cm²) throughout all depositions. ZnS-SiO₂-CeO₂ (85 : 13 : 2 at ratio) was used as an inert protection layer in some cases and deposited from a respective target at 500 W.

Transmission infrared spectra of the sputtered layers on silicon substrates were measured over the range of 400 cm⁻¹ to 4000 cm⁻¹ using a vacuum Fourier-transform IR spectrometer (BOMEM DA 3.36) at a resolution of 1 cm⁻¹. Powder standards of commercially available silver oxides AgO (Fluka, purum >98% and Aldrich, declared as predominantly AgO, remainder Ag₂O) and Ag₂O (Kanto Chemicals, >99% purity) were recorded as Nujol mull.

Micro Raman measurements of the sputtered layers on silicon were carried out with a Renishaw Raman scope equipped with an argon-ion-laser ($\lambda = 488$ nm) in backscattering geometry. Spectra of the silver oxide powder standards were recorded on pressings. The laser power was adjusted to 300 μ W on the sample surfaces and the samples were ice cooled and measured under nitrogen atmosphere to avoid light induced changes in the layers. Detection times of 10 s together with 100 accumulations per run compensated poor signal to noise ratios.

Optical transmission changes of sputtered AgO_x layers on slide glass as a function of temperature were measured through an optical microscope with connected photodetector at a wavelength of 635 nm. All sample films were heated by a LINKAM LK-600PM micro-heating stage from room temperature to 450 °C with a ramp rate of 30 °C/min.

The dynamic nonlinearities of disk samples were evaluated by a DDU-100 disk drive tester (Pulsetec. Ind. Co. Ltd.) with a laser wavelength of 635 nm and an objective lens numerical aperture of 0.6. For this case a 15 nm AgO_x layer was deposited on a polycarbonate disk blank sandwiched by ZnS-SiO₂-CeO₂ layers of 20 nm and 130 nm thickness.

The refractive indices of all films were measured with a DHA-OLX/S4M MIZOJIRI ellipsometer at a wavelength of 632.8 nm.

3. Results and Discussion

In the following discussion, we describe optical characteristics of the deposited AgO_x-films obtained at a particular f_r , where f_r is expressed as the sputtering gas mixture ratio of the oxygen flow and the total flow

Fig. 1 Complex refractive indices of AgO_x layers as a function of oxygen concentration in the sputtering gas mixture.

of oxygen and argon according to

$$f_r = f[\text{O}_2]/(f[\text{Ar}] + f[\text{O}_2]).$$

The individual flow of the gases was adjusted by use of mass flow controllers and the total flow was always 20 sccm.

Figure 1 shows the measured complex refractive index of the AgO_x-layers as a function of the oxygen content f_r . The graph shows a characteristic run for rising oxygen concentration in the AgO_x layers. At $f_r = 0$, corresponding to pure silver, the refractive index is $n = 0.08 + 3.98i$. For increasing oxygen concentrations up to $f_r \approx 2.5$, the real part rises to 2.79 whereas the imaginary parts drops to about 0.31, indicating the presence of a highly transparent silver oxide film. Further oxygen increase leads to an immediate rise of the imaginary part and a stabilization at a value of 1.7i whereas the run of the real part is only slightly affected.

To verify the layer composition at a particular f_r , IR spectroscopy was carried out. Probed films except pure Ag (with $f_r = 0$) showed always one broad band situated between 523 cm⁻¹ and 535 cm⁻¹. No systematic variation with oxygen concentration could be found except that commercially available Ag₂O and AgO standards exhibited peaks at slightly higher wave number around 445 cm⁻¹. We reduce the observed shift of the deposited films to stress effects, imperfections and impurities⁵⁾ which can always be found in reactively sputtered AgO_x-layers. Our results for a film with $f_r = 0.25$ are in accordance to IR measurements of Slager et al.⁶⁾ who investigated evaporated Ag films after oxidation to Ag₂O in O₂ and O₃ (one band at 535 cm⁻¹). To our knowledge no IR-data concerning any AgO samples are published in the literature as yet.

Fig. 2 Raman spectra of AgO_x layers obtained by sputtering with different O_2 content f_r .

Complementary Raman spectroscopy was applied to substantiate the latter results. The spectra for selected films obtained under ice cooling and nitrogen flow of the samples are shown in Fig. 2. The layer with $f_r = 0$ shows, in agreement to bulk Ag, no Raman peaks in the region between 110 cm^{-1} and 2000 cm^{-1} . For $f_r = 0.25$ no specific Raman peaks can be found but the characteristic silicon band at 520 cm^{-1} is clearly visible due to the high transparency of such films as pointed out in the previous discussion of the refractive indices. It has already been verified by Hamilton et al.⁷⁾ that electrochemically generated Ag_2O is not Raman active due to symmetry reasons of the crystal lattice. In the spectra of $f_r = 0.5$ – $f_r = 0.88$ distinct peaks at about 430 cm^{-1} , 470 cm^{-1} , 490 cm^{-1} and 220 cm^{-1} appear with different intensities and confirm the spectra obtained by Hamilton et al.⁷⁾. These peaks can be assigned to the monoclinic crystal lattice of AgO. Raman spectroscopy of powder standards re-confirmed the peak positions for AgO and respective the lack of peaks for Ag_2O .

However in case the samples were not cooled two additional broad and intense peaks at about 1380 cm^{-1} and 1600 cm^{-1} increasingly developed with accumulation time. These huge peaks could not be assigned to any vibration mode occurring in silver compounds. Since the deposited films undergo visible changes in the form of specular spots at the laser position, we suppose

Fig. 3 Optical transmission of sputtered silver oxide layers as a function of temperature.

that the sudden appearance of both features is related to the formation of silver droplets in combination with carbon residues⁸⁾ on their surfaces.

Empirical investigations of super-RENS disks revealed that the structure starts to work as a mask layer when the AgO_x -films are sputtered above a minimum oxygen concentration of $f_r = 0.25$ required for the formation of an Ag_2O phase as main constituent. A further increase of the oxygen concentration and a simultaneous increase in the AgO fraction shows only little influence on the super-RENS resolution characteristics. For reasons of the stability of the deposition process those disks are usually sputtered at $f_r = 0.5$.

Since it is believed that the light scattering center super-RENS effect is based on the photo-thermal generation of small silver clusters, we investigated the decomposition pathway of the AgO- and Ag_2O - rich phases by measuring the optical transmission as a function of sample temperature. Results for layers with $f_r = 0.25$, 0.5 and 0.75 are given in Fig. 3. The different initial transmission of the films is due to the specific refractive indices of the samples. The transmitted light intensity of the Ag_2O sample obtained at $f_r = 0.25$ decreases monotonically with increasing temperature while the AgO containing films (deposited at $f_r = 0.5$ and $f_r = 0.75$) show a sudden increase in transmission at certain temperatures above 100 °C followed by a decrease at a common temperature of about 170 °C . We explain this behavior with the decomposition of AgO into the highly transparent Ag_2O and oxygen. Further heating results in the decomposition of Ag_2O into Ag and O_2 . The lower onset temperature for the $f_r = 0.5$ -layer might be due to nucleation sites, i.e., already present Ag_2O sites and silver particles⁹⁾ that catalyze the decomposition. All samples showed zero transmission at 450 °C indicating the presence of silver

Fig. 4 Reflected light intensity of a super-RENS mask layer deposited at $f_r = 0.5$ as a function of disk rotations (at 6 m/s) measured by an optical disk drive testing unit.

as the dominant component.

The formation of Ag_2O as the initial step can be reconfirmed by dynamic measurements of disk samples. The curves in Fig. 4 show the reflection outputs of the disk drive tester using a disk structure of polycarbonate/ $\text{ZnS-SiO}_2\text{-CeO}_2$ (20 nm)/ AgO_x (15 nm, $f_r = 0.5$)/ $\text{ZnS-SiO}_2\text{-CeO}_2$ (130 nm) as a function of disk rotations or exposure time of a disk track to the laser. The initial reflection first drops due to the transition of AgO into Ag_2O and then gradually increases owing to the final formation of Ag scattering centers. This behavior matches the increased transmission of the sample obtained at $f_r = 0.5$ shown in Fig. 3. It should be pointed out that this slow response is not observed in super-RENS experiments. If a highly absorbing storage medium is deposited in the vicinity of the silver oxide layer, silver scattering centers are the immediate product of laser-induced write-and-read-out reactions. Since magneto-optical or phase change layers act like a heat depot the decomposition reaction is accelerated and intermediate Ag_2O formation is no longer detectable.

4. Conclusions

Reactively sputtered silver oxide layers at different oxygen concentrations were probed by spectroscopic methods. Raman spectra provided evidence for Ag_2O when the deposition is carried out in a poor oxygen gas mixture ($f_r = 0.25$) and for AgO ($f_r = 0.75$) in an oxygen rich gas mixture. In the latter case a characteristic band at 432 cm^{-1} proves the presence of AgO that vanishes when the oxygen concentration is diminished below ca. $f = 0.4$. The film composition changes gradually between the two oxygen concentrations, leading to films composed of mixtures of Ag_2O and AgO phases. Super-RENS layers (deposited at $f = 0.5$) could therefore be identified to be a mixture of Ag , Ag_2O and AgO . Heating up those layers results in a decomposition/transition reaction with initially medium light transmission due to AgO followed by a strong increase (lower imaginary part of n for Ag_2O) and a final drop when only Ag is present.

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