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## Investigations of Sputtered Silver Oxide Deposits for the SUPER-RENS High Density Optical Data Storage Application

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### ABSTRACT

Thin silver oxide films used as mask layers in super-Resolution Nearfield Structure (super-RENS) disks for high density optical data storage were reactively sputter-deposited and their composition was determined by spectroscopic means. We found that the stoichiometry of the films changed with the oxygen content in the sputtering gas atmosphere. With a stepwise increase in the percentage of  $O_2$  from 0 - 100%, the corresponding layers consist of Ag, mixtures of Ag and  $Ag_2O$ ,  $Ag_2O$ , mixtures of  $Ag_2O$  and AgO and AgO. Laser activation of such oxidic phase containing deposits results in the decomposition of the material and excitation of strong local plasmons in the remaining silver clusters. This was confirmed by acquiring surface enhanced Raman spectra (SERS) of benzoic acid (BA), copper phthalocyanine (CP) and internal carbon impurities on silver oxide substrates. From this data, we conclude that the sub-wavelength resolution obtained in super-RENS disks is mediated by local surface plasmons on small silver particles forming in the mask layer.

### INTRODUCTION

Super-RENS is a promising technique to achieve high density optical data storage. The light scattering center-(lsc-)super-RENS disk (1), developed in 1999 uses a silver oxide mask layer in close proximity to a phase change storage layer to overcome the diffraction limit in conventional optical data storage applications. Kim et al. (2) recently showed that the application of a silver oxide mask layer in combination with a magneto-optical storage layer also enables the generation of marks with dimensions well below the diffraction limit. Figure 1 displays the general super-RENS layer structure together with a comparison of CNR against mark size for the respective structure and a conventional phase-change disk. The applied readout power as well as the required recording power is generally higher in the super-RENS case to obtain the maximum signal resolution. However, the mechanism of LSC super RE NS is still under discussion. Recent studies (3) supported the suggestion that the super resolution effect is mediated by strongly scattering local surface plasmons which are stimulated on Ag particles in the mask layer. These Ag clusters are photothermally generated through the decomposition of silver oxide to silver and oxygen. During the read out process, the impinging laser beam excites the Ag particles and simultaneously produces optical near fields on the marks in the recording layer. The

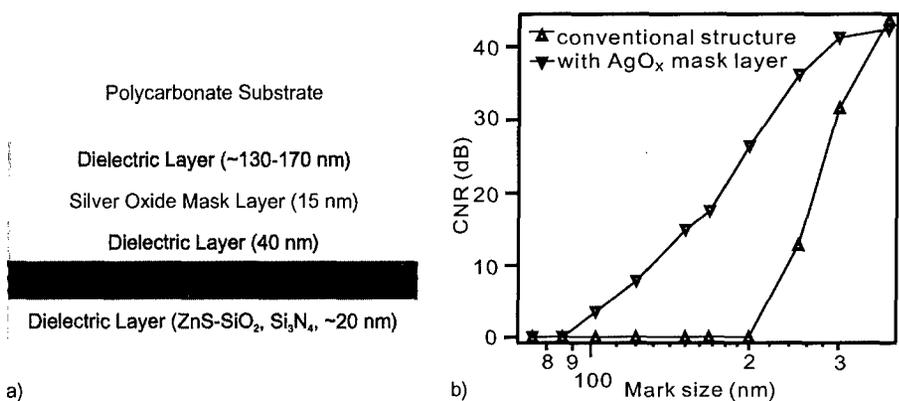


Figure 1. a) Schematic structure of a lsc-super-RENS disk. b) Mark size and correlated CNR for a lsc-super-RENS disk (readout power 3.5 mW) and a conventional optical disk (readout power 1.5 mW). Laser wavelength was 635 nm, NA 0.6 and constant linear velocity was 6 m/sec.

superposition of these laterally confined fields with the local plasmons on the adjacent Ag particles is then thought to give rise to the observed sub-wavelength resolution.

The intention of this work is to gather chemical and optical characteristics of sputtered silver oxide layers for a better understanding of the decomposition pathway and the eventual excitation of local plasmons in emerging silver clusters. It was suggested (3) that local surface plasmons contribute to the enhanced CNR in super-RENS experiments, hence the interaction of such layers with suitable molecules should give rise to surface enhanced Raman scattering (SERS) (4; 5). To prove this, silver oxide layers are produced by reactive sputtering with parameters resembling those of the super-RENS disk fabrication, however, the oxygen concentration in the sputtering gas mixture was varied from 0 to 100% to obtain layers composed of different phases. These layers were probed by Raman spectroscopy and the complex refractive indices were measured.

## EXPERIMENTAL

Silver oxide films were deposited by reactive r.f. magnetron sputtering of a 3-inch Ag target (99.999% purity) on either glass slide or polished silicon wafers. Layers of different composition were obtained by changing the gas ratio of O<sub>2</sub> and Ar. Details are given in reference (6). The flow of individual gases was adjusted by mass flow controllers such that a total flow of 20 sccm was maintained. Since the deposition rate changed with varying oxygen content, the sputtering time was always adjusted to obtain films of either 300 nm thickness for the subsequent layer characterization, or of 15 nm thickness to imitate super-RENS conditions during the SERS experiments. 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/cm<sup>2</sup>) throughout each deposition.

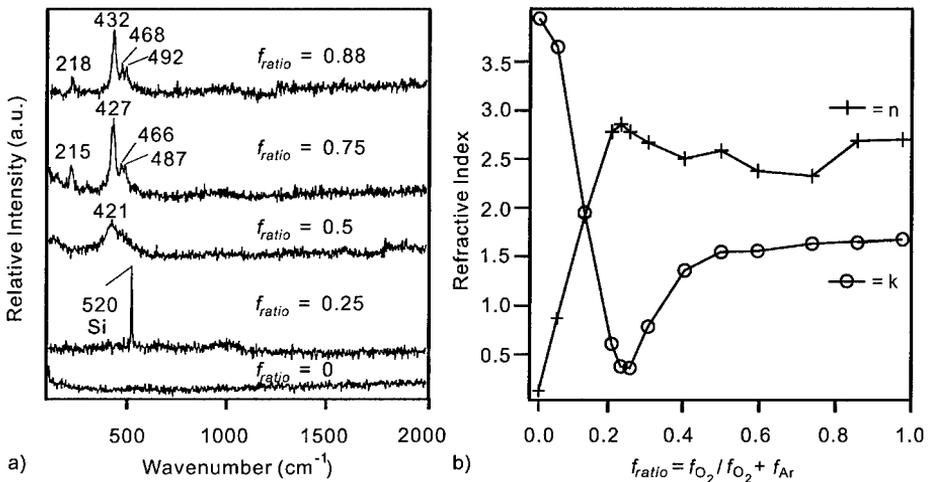


Figure 2. a) Raman spectra of AgO<sub>x</sub> layers obtained by sputtering at different  $f_{ratio}$ . b) Complex refractive indices of AgO<sub>x</sub> layers as a function of oxygen concentration in the sputtering gas mixture.

Micro Raman measurements of the sputtered layers on silicon were carried out with a Renishaw Ramanscope equipped with an argon-ion-laser ( $\lambda = 488$  nm) in backscattering geometry. The laser spot size at the sample surface was diffraction limited and estimated to be  $\approx 2$   $\mu$ m. The laser power was adjusted to 300  $\mu$ W 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 for poor signal to noise ratios. Powder samples of commercially available silver oxides AgO (Fluka, Aldrich) and Ag<sub>2</sub>O (Kanto Chemicals), benzoic acid (Kanto Chemicals), copper phthalocyanine (Aldrich) as well as high purity carbon pressings (Kojundo Chemical Laboratory) and 2-propanol (Fluka) were used to confirm reference Raman spectra of the respective compounds.

SER spectra of benzoic acid were acquired by immersing a AgO sample into 10 mL of a  $10^{-4}$  M benzoic acid/2-propanol solution. In the case of copper phthalocyanine, a film several monolayers thick was evaporated directly onto AgO. The resulting intense SER spectra were recorded with an excitation power of 400  $\mu$ W and 5 s integration time.

Refractive indices of the films were measured with a DHA-OLX/S4M MIZOJIRI ellipsometer at a wavelength of 632.8 nm.

## RESULTS

In the following discussion, we describe characteristics of the deposited AgO<sub>x</sub>-films obtained at a particular  $f_{ratio}$ , whereby  $f_{ratio}$  is expressed as ratio of the oxygen flow and the total flow of oxygen and argon in the sputtering gas mixture according to the equation

$$f_{ratio} = f_{O_2}/(f_{Ar} + f_{O_2}).$$

Raman spectroscopy was carried out to determine the layer composition. Spectra of layers with selected  $f_{ratio}$  were obtained in nitrogen flow under intensive cooling of the samples and are shown in figure 2 a. It was necessary to apply those precautions, since without them the silver oxide films readily underwent decomposition as a result of interaction with the laser beam. The laser intensity had to be adjusted carefully to compromise between the very low Raman scattering cross section of the silver oxides and their tendency to decompose. Layers obtained at  $f_{ratio} = 0$  showed in agreement to bulk Ag no Raman peaks in the region between  $110 \text{ cm}^{-1}$  and  $2000 \text{ cm}^{-1}$ . For  $f_{ratio} = 0.25$  no specific Raman peaks can be found but the characteristic band of the silicon substrate material at  $520 \text{ cm}^{-1}$  is clearly visible due to the high transparency of such films (discussed below). Hamilton et al. (7) verified that electrochemically generated  $\text{Ag}_2\text{O}$  is not Raman active due to the symmetry of the crystal lattice but assigned bands at about  $220 \text{ cm}^{-1}$ ,  $430 \text{ cm}^{-1}$ ,  $470 \text{ cm}^{-1}$ ,  $490 \text{ cm}^{-1}$  to  $\text{AgO}$ . Our layers deposited in the range between  $f_{ratio} = 0.5$  and  $f_{ratio} = 0.75$  showed the same characteristic bands with increasing intensities for increasing oxygen concentration.

The assignment of specific oxidic phases to distinct  $f_{ratio}$  values was substantiated by measurements of complex refractive indices of the layers. Figure 2 b shows values obtained for  $n$  and  $k$  as a function of the oxygen concentration during the deposition. The graphs show a characteristic run for rising oxygen content in the  $\text{AgO}_x$  layers. For pure silver, the refractive index was measured to be  $n = 0.08 + 3.98i$ . For increasing oxygen concentrations up to  $f_{ratio} \approx 0.25$ , the real part increases to 2.79 whereas the imaginary parts drops to about  $0.31i$ , indicating the presence of a highly transparent silver (I) oxide ( $\text{Ag}_2\text{O}$ ) film (10) in accordance to the previously described Raman measurements. Further oxygen addition leads to an immediate rise of the imaginary part to  $1.7i$  where it stabilized, while the values for the real part changed only slightly. The results are summarized in table I.

However, when samples were not cooled while Raman spectra acquisition proceeded, they underwent visible changes at the laser position in form of specular spots. Simultaneously, two additional broad and intense peaks at about  $1380 \text{ cm}^{-1}$  and  $1580 \text{ cm}^{-1}$  developed and soon dominated the spectrum. These huge peaks have often been observed while performing SERS on suitable silver samples and have been assigned to amorphous carbon (8) or nanocrystalline carbon residues (9) on their surfaces. In our case, carbon traces were incorporated during the deposition process. Figure 3 a shows typical examples of such spectra obtained on different silver oxide substrates. The time dependent development of the SERS intensities in each individual spectrum was different. In case of  $\text{Ag}_2\text{O}$  ( $f_{ratio} = 0.25$ ), the surface enhanced peaks were immediately formed whereas layers with higher oxygen content needed a longer activation time. Above a certain threshold

Table I. Layer composition as a function of oxygen flow ratio

$f_{ratio}$	0	0.175	0.25	0.5	0.75
Layer Composition	Ag	Ag + $\text{Ag}_2\text{O}$	$\text{Ag}_2\text{O}$	$\text{Ag}_2\text{O} + \text{AgO}$	AgO

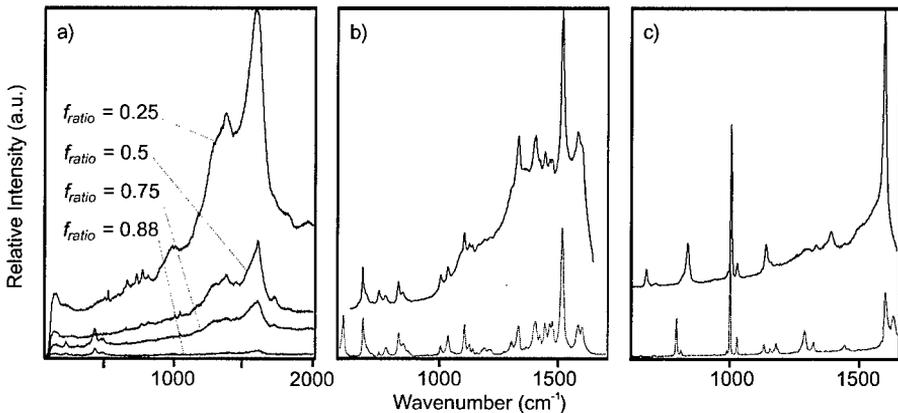


Figure 3. a) SERS of layer-internal  $\alpha$ -carbon impurities and benzoic acid (b)/copper phthalocyanine (c) on silver oxide films. The dotted curves are conventional Raman spectra of powder standards shown for comparison.

power, all layers showed comparable activity. Obviously, layers with a smaller oxygen content decompose faster than oxygen rich phases, probably due to silver nucleation sites which are already present in the film. To check for the potential feasibility of the sputtered films to SER spectroscopy, we applied several external chemicals to the layers and recorded the resultant spectra. It turned out that the activated surface is suitable to amplify Raman bands of a variety of low concentrated compounds. Figure 3 b and c shows examples of SER spectra (solid lines) of evaporated copper phthalocyanine and of a  $10^{-4}$  M benzoic acid solution. For comparison, conventional Raman spectra of corresponding powder samples (dotted lines) are also shown. BA and CP were applied to the silver oxide layers in concentrations that are not detectable by conventional Raman spectroscopy but produced a clear and intense SER signal. The observed shifts in specific SERS peak positions and intensities depend on the interaction of the molecules and the silver oxide surface. The bonding of functional groups to the substrate influences the symmetry of the molecule as well as the intermolecular distances and leads to characteristic shifts and/or the appearance of previously forbidden bands in the spectra. A detailed discussion can be found in the SERS review of Moskowits (11).

There is general agreement that a major contribution to SERS effects is achieved by strongly scattering local surface plasmons on specific substrate materials. Our results support the hypothesis that activated silver oxide layers, as applied in super-RENS disks, could provide a mark signal amplification by electromagnetic field enhancement.

## Conclusions

Reactively sputtered silver oxide layers were probed by Raman spectroscopy and the complex refractive indices were measured. The results indicated that the main constituents

gradually change from Ag over Ag<sub>2</sub>O to AgO with increasing oxygen content in the sputtering gas atmosphere. Raman spectra of cooled thin films provided a characteristic band at 432 cm<sup>-1</sup> as proof of the presence for AgO. Layers deposited at low oxygen concentration with a refractive index of  $n = 2.79 + 0.31i$  were determined to be composed of Ag<sub>2</sub>O. Super-RENS mask layers, deposited at a medium oxygen concentration could be identified as a mixture of Ag<sub>2</sub>O and AgO. Furthermore, we found that thin oxide layers readily decompose to silver particles and oxygen upon photothermal activation. The silver clusters sustain strong local surface plasmons and change the substrates to effective surface enhanced Raman spectroscopy substrates. This was proofed by the development of characteristic SERS peaks of layer-internal  $\alpha$ -carbon trace impurities, diluted benzoic acid/2-propanol solutions and evaporated copper phthalocyanine.

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