Ferroelectrics of Chalcogenides and Optical Super-Resolution

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Abstract

Since very recent study, GeSbTe and AgInSbTe have been thought as *ferroelectric materials*, especially under strain-force condition. The *ferroelectrics* of the films strongly appear when sandwiched by ZnS-SiO_2 films. It turned out that the super-resolution effect of super-RENS discs using PtOx is related to a transition temperature of the *2nd phase transition* and *ferroelectric properties*. In this paper, we reveal the *super-RENS* readout mechanism in *ferroelectric catastrophe.*

Keywords: Super-resolution near-field structure (super-RENS), ferroelectrics, ferroelectric catastrophe, chalcogenides, GeSbTe, AgInSbTe, strain force, 2nd phase transition.

INTRODUCTION

Recently, the feasibility studies for the next generation optical memory beyond blue-ray and HD-DVD disc have been increasing worldwide. Two novel recording systems have especially been attractive: optical near-field recording (NFR) and holographic recording. NFR is now sub-divided into two types: using flying head with a solid immersion lens (SIL) and using super resolution (SR) in optical discs.[1-5] The former method is clearly based on the theory in physics and optics, and the mark resolution and technical limitation are rigidly determined. In the later type, in contrast, the resolution mostly depends on material itself. Although the most advanced super-resolution near-field structure (super-RENS) disc shows more than 40-dB CNR at 50-nm pits [6], nobody knows how small pit is theoretically recorded and resolved in SR-disc technology. Kikukawa *et al.* first mentioned the importance of heat generated in SR materials by ROM-discs (super-ROM). [7] It was confirmed that almost semiconductive materials, for examples, Si, Ge and W show SR effect. However, there exists a specific difference in between super-ROM and super-RENS. The SR of these semiconductive films has no threshold or sharp transition against laser power in readout, while in super-RENS consisting of AgInSbTe, a clear transition power is confirmed. Furthermore, the signal intensity of pits smaller than 100 nm is very huge in comparison of super-RENS discs with any other materials. At glance both SRs look similar, but it would be due to different physical principles. For the last couple of years, we have engaged in revealing the readout mechanism besides increasing the signal intensity and resolution. In this paper, we are going to discuss the relationship between the super resolution and *ferroelectric transition* with so-called *2nd phase transition* in detail.

CHARACTERISTICS OF PLATINUM-OXIDE SUPER-RENS DISC

Before the discussion, let's summarize the significant differences in between the PtOx-super-RENS disc and the other super-RENS discs with an Sb or AgOx layer. The PtOx layer no longer works as a light-masking layer with an aperture in SR readout because of the irreversible chemical reaction: decomposition, at first. The chalcogenide film of AgInSbTe or GeSbTe plays a role in the active layer instead. Secondly, the SR threshold power in readout no longer depends on the pit size, while the power in the Sb-super-RENS disc has to precisely be adjusted to every pit size to obtain the best signal intensity.[3] In addition, a sharp drop in the intensity profile is allowed at a specific pit size. This is thought as evanescent field interference in between a small aperture generated in the Sb thin layer and pit pattern recorded in the chalgonenide layer. This drop is a fatal disadvantage of the aperture-type super-RENS discs. Thirdly, the sharp threshold power in readout does not shift for short and long pits. All the characteristics generated in the Sb super-RENS disc can be explained by simple Fourier optics or by more complex FDTD computer simulations with a simple aperture model. However, this model can never be applied to the behavior of the PtOx super-RENS disc at all. It is hard to understand from the model that a small aperture with a 1/100 area to the laser spot generates more than 40-dB CNR because available photon numbers from the aperture would be very small in comparison to the others bouncing back from the other masked area (99/100). Forth, the SR effect does not depend on laser wavelength in readout. In both using red (635-nm wavelength) and blue laser (405 nm), it has already been confirmed that the signal enhancement and resolution only depend on the beam spot size on the disc surface. [4,5] This phenomenon is very attractive for terabyte memory. Once the super-RENS disc and SIL pickup are combined together in one system, ~20-nm pits would be recorded and read out with more than a commercial signal level (> 40 dB) in principle. The last, the strong SR effect has only been observed in dynamic tests, but not clearly seen by static. This means that the strong electrical field in the laser beam spot may assist or induce the SR effect as well as temperature. This is very interesting on the point of view of depending on the electromagnetic field.

REFRACTIVE INDEX AND FERROELECTRICS

In order to explain all the characteristics, a refractive index in the local area (that is, active region) must have a extremely huge value against any other area otherwise the scattered signal photons are almost covered over the major photons bounced back from the masked area. One of physical phenomena to induce the index change is the *Kerr effect*. This phenomenon is well known as the optical nonlinearity of the 3rd order, in which the index linearly changes with the laser intensity. However, the deviation induced by the effect is not so large in comparison to that observed in the super-RENS disc and the sharp threshold power in the SR cannot be explained. The 2nd order may generate a *SHG* waves. However, the experimental results by Kim *et al.* denied it because of the observation of 80-nm pit patters with 40-dB CNR by a disc drive system with 635-nm wavelength and NA 0.60: the theoretical resolution limit by the SHG must be 132 nm.[5] Therefore, 2nd and 3rd order optical nonlinearities are little related to the SR of the super-RENS disc.

In turning around to classical physics, refractive index n is expressed by *electronic polarizability* α with the *Clausius-Mossotti* equation. In quantum physics, the equation (1) is further modified by the summation of oscillator strengths attributed to each band transition (2).

$$\alpha_\infty = \frac{3}{4\pi N_A}\frac{n_\infty^2 - 1}{n_\infty^2 + 2}V \tag{1}$$

$$\alpha_m = \sum_k \frac{2e^2\omega_{mk}\langle m|\hat{r}|k\rangle\langle k|\hat{r}|m\rangle E_0\cos(\omega t)}{(\omega_{mk}^2 - \omega^2)\hbar} \tag{2}$$

Hence in equation (1), α_∞ and n_∞ are the *electronic polarizability* and refractive index at the wavelength ->∞. N_A and V are the *Avogadro number* and volume in a medium. In equation (2), equation (1) is modified by the summation of the contributions from each band-transition m<->k. Hence, ω, ω_{mk}, e, $e\hat{r}$, E_0 are applied electrical frequency, resonance frequency between the bands, electron charge, electron displacement (that is, $e\hat{r}$ is *dipole operator*), and applied electric field, respectively. In solid or liquid, $\frac{3V}{4\pi N_A}$ in equation (1) may set at a constant ρ, and equation (1) is further simplified to,

$$n^2 = \frac{2\alpha + \rho}{\rho - \alpha} \tag{3}$$

Hence, ρ is thought as something like a space freedom at around the local position of each atom in the unit cell. When $\rho \sim \alpha$, n^2 may diverse and take a huge value close to the singular point. *Ferroelectrics* is well known to show such a behavior to temperature with a transition so-called the Curie temperature T_c. It is also known that GeTe holds the *ferroelectric characteristics* with the 2nd phase-transition at Tc~352°C. [8,9] The Raman soft-mode phonons accompanied by the ferroelectric effect were actually observed at around 3.5 THz ($110 cm^{-1}$), and the source is attributed to the Te local-displacement in the unit cell. Yamada *et al.* mentioned the crystalline lattice deformation of $Ge_2Sb_2Te_5$ (hereafter *GST*) and $Ag_{3.4}In_{3.7}Sb_{76.4}Te_{16.5}$ (hereafter *AIST*) systems with respect to temperature. They discovered relatively very large space deviations at the Sb and the Ge sites *4(b)*, in comparison to the Te site *4(a)* in the *NaCl-type fcc* unit lattice of GeSbTe.[10] It turned out that the lattice transforms into another *hexagonal* lattice at ~260°C. On the other hand, AIST retains the hexagonal lattice (A7 belong to $R\bar{3}m$), which is similar to the original Sb lattice with the c-axis expanding from 11.2 to 11.6 A at temperature up to 350°C. More than the temperature, the lattice transforms into *R3m rhombohedral*. These results support that AIST may also show a 2nd phase-transition more anisotropically than that of the GST system. So far, a large amount of studies have revealed the transition temperatures of optical phase-change alloys. However, most of all were only focused on the 1st phase transitions: a transition in between as-deposited amorphous and crystal, and the melting points. None of them has taken care of 2nd phase-transition because of its tiny discontinuity on heat flow in DSC and too small optical change on reflectivity or transmittance in macro-scale.

In early 2004, we proposed a readout model of the PtOx super-RENS disc by the effect of the ferroelectric properties of the AIST and GST thin films on *Natontechnology* **15** (2004) 411-415. [11] Hence, the SR effect is only active at a very narrow transition temperature in the *ferroelectric catastrophe*. In the paper, we experimentally determined the relationship between the readout laser power and disc temperature, and clear revealed that the threshold laser power emerging the SR in the super-RENS discs are well agreed with the 2nd phase-transition temperatures. Here, we consider the relationship between the ferroelectrics and the SR effect in much more detail by the *Landau theory*. In the Landau theory of the ferroelectrics, it is assumed that the free energy F_p is decomposed into the power series of the dipole P. Because F_p has to get energy minimums against P, it is only made of the even series of P.

$$F_P = \tfrac{1}{2}\alpha P^2 + \tfrac{1}{4}\beta P^4 + \tfrac{1}{6}\gamma P^6 + ... \tag{4}$$

Hence, $\alpha = \alpha_0(T - T_0)$ and $\alpha_0 > 0$. Also, we put $\beta > 0$.
Now, as we are going to find the energy minimums of $F_{p,}$ the first derivative $\frac{dF_p}{dP} = 0$.
Thus, we can obtain;

$$\begin{aligned} &\tfrac{\partial F}{\partial P} = \alpha P + \beta P^3 + \gamma P^5 = E = 0 \\ &\tfrac{\partial^2 F}{\partial P^2} = \tfrac{\partial E}{\partial P} = \chi^{-1} \\ &4\pi\varepsilon^{-1} = \tfrac{\partial E}{\partial P} = \alpha_0(T - T_0) + 3\beta P_s^2 = 2\alpha_0(T_0 - T) \end{aligned} \tag{5}$$

χ in the second equation of (5) is a dielectric *susceptibility* and $P=\chi E$. Here, we neglected the higher orders more than the second derivative. As a result, we can obtain the famous relationship of the Curie temperature.

$$\varepsilon \propto (T_0 - T)^{-1} \tag{6}$$

In optical discs, however, an as-deposited amorphous film must be once crystallized before recording. In the process, the film volume is reduced more than 5% from the original condition. The reduction is in isotropic; that is, the protection layers sandwiching the phase-change film induce a high strain force (Actually, the strain force is not in isotropic but anisotropic) because the crystallization procedure is usually carried out along the tracks and the groove structure may modify or block the strain force across the tracks. From our previous experiment with a ZnS-SiO_2/Sb/ZnS-SiO_2, the strain force is roughly estimated 20~40MPa.[12] As increasing temperature, the crystalline growth is further accelerated with fatting the grain size. Finally, the volume change is balanced in between the thermal expansion and the reduction due to the crystalline growth. Therefore, it easy turns out that equation (4) is not applicable to the conditions including the strain. Instead equation (4) is modified including uni-axial strain force (More in general, we have to consider by-axial force) and its coupling term with the dipole.

$$F_P = \tfrac{1}{2}\alpha P^2 + \tfrac{1}{4}\beta' P^4 + \tfrac{1}{2}c\left(x - x_0\right)^2 + qxP^2 \tag{7}$$

The third term is for the strain and the forth one is for the coupling. Hence, c, x_0 and q are a *Young's module*, the original position of an atom, in which $\Delta x = (x - x_0)$ means $\sim\rho^{1/3}$ of equation (3), and a coupling constant, respectively. Here, in addition to the local minimum of F_p to P, we obtain another minimum by displacement x.

$$\tfrac{\partial F}{\partial x} = 0 \tag{8}$$

As a result, now we can obtain an attractive relationship between the displacement $\Delta x_s = (x - x_0)$ and P_s.

$$\Delta x_s = -qP_s^2 / c \tag{9}$$

The *self-distortion* now may induce the dipole. Alternatively, the large electrical dipole may induce a very large displacement in the unit cell by the *Yield point*, resulting in plastic deformation, material flow, or transition to more energetically stable crystalline state. At the transition point, refractive index theoretically has no meaning or no value. This ferroelectric catastrophe probably is the readout mechanism of super-resolution in super-RENS disc.

SUPER-RESOLUTION MODEL OF PLATINUM-OXIDE SUPER-RENS DISC

Here, let's more simplify a PtOx super-RENS disc structure with a single AIST layer sandwiched by two ZnS-SiO$_2$ layers. Even after the all film deposition, the AIST layer holds amorphous. In recording, whether the layer is in amorphous or crystal is not a problem because the recording track is almost all crystallized by the pulsed laser beam except for recording longer pits with more than the resolution limit. It means that the track is only crystallized and the layer volume is reduced ~5% as a result. The ZnS-SiO$_2$ protection layers top and bottom must have a force balance with the crystallized layer, inducing a strong tensile stress to the AIST at this moment. Finally, the disc is deformed upwards or sometimes twisted as shown in **Figure 1**.

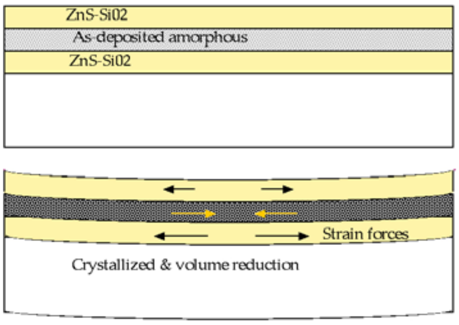

Figure 1 Top: simple structure with multilayer of optical recording and bottom: it after recording or initialization (crystallization). By the volume reduction, the disc is bended and large strain forces are induced at the interface between ZnS-SiO$_2$ and AIST or GST.

In readout, as increasing the laser power: temperature, further crystallization with the growth and volume reduction proceeds against the thermal volume expansion by T_0 ~350°C. During the process, an additional physical phenomenon may occur. Because of the semiconductivity of the crystal, a large amount of carriers are generated in the laser spot area, and diffuse outwards (see **Figure 2**). However, due to the anisotropic crystallization and strain force, a static electrical field is generated along the track direction. This effect was recently confirmed by Nakano *et. al.*.[13] The induced static dipole further assists the deformation to the yield point of the first crystalline phase.

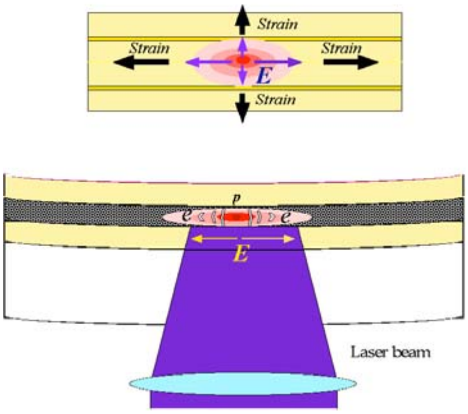

Figure 2 Carrier generated in the AIST or GST by focusing and increasing the incident laser beam. The strain force may generate anisotropically static field.

At ~350°C, the threshold in the Free-energy, the first crystalline phase cannot endure its unit lattice and probably allow to transit into another stable phase: 2nd phase-transition. Only in a very narrow temperature region in the laser spot at $\alpha \sim \rho$, the refractive index n becomes discontinuous and diverse, resulting in optical super resolution. If this model is true, the transition edge plays a crucial role in the SR, in which the resolution is determined the edge width.

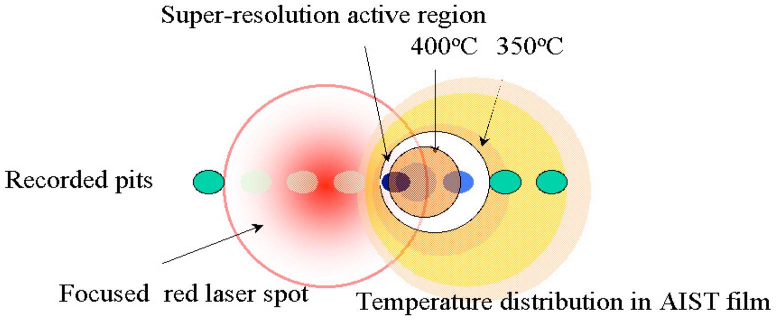

Figure 3 The readout model of PtOx super-RENS disc by ferroelectric catastrophe.

This model suggests that recorded pits smaller than the diffraction limit are read out by the edge, while longer pits than the limit are reproduced by both the edge and far-field diffraction (see **Figure 3**). This model can well explain that the CNRs of small and large pits (but beyond the diffraction limit) are almost constant with more than 40 dB by less than 50-nm size. Furthermore, the threshold power: temperature only depends on the intrinsic properties of materials and on the strain force field induced by surrounding materials. In addition, it is explained that without the electrical field attributed to the high intensity laser power, this SR is hard to be observed experimentally.

SUMMARY

The SR of the PtOx-super-RENS disc is probably attributed to the ferroelectric catastrophe induced by the strain force balance with the protective layers. We believe that the chalcogenides, especially GST and AIST give us much more attractive aspects not only for the 1st phase-change application to the optical disc and static memory, but also for future nanotechnological devices based on the 2nd phase-change behavior.

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