

## Enhancement of Data Transfer Rate of Phase Change Optical Disk by Doping Nitrogen in Ge–In–Sb–Te Recording Layer

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(Received November 12, 2003; accepted April 16, 2004; published August 10, 2004)

This work investigated the enhancement of the data transfer rate and/or recrystallization speed of Ge–In–Sb–Te recording material by nitrogen doping. The effects of nitrogen content on the dynamic properties of optical disks and the corresponding microstructural changes of the recording layer were studied. The experimental results showed that nitrogen doping at a sputtering gas flow ratio of  $N_2/Ar = 3\%$  might enhance the data transfer rate of an optical disk up to 1.6 times without severely damaging the signal jitter values. However, the disks failed the dynamic tests when too much nitrogen ( $N_2/Ar \geq 5\%$ ) was introduced. Dynamic testing also revealed that nitrogen doping slightly increased the noise level and jitter of the disks. Transmission electron microscopy (TEM) found that nitrogen doping promoted a phase transformation by generating numerous nucleation sites uniformly distributed in the recording layer and hence increased recrystallization speed.

[DOI: 10.1143/JJAP.43.5316]

KEYWORDS: Ge–In–Sb–Te recording material, data transfer rate, recrystallization speed, nitrogen doping

### 1. Introduction

The development of optical disks using phase change materials as the recording media is always geared a large storage capacity and a high data transfer rate. Currently the eutectic Sb–Te system, called the fast-growth phase change material, has received much attention because it results in good signal properties and a high recrystallization speed when short-wavelength lasers and high-numerical-aperture (NA) lenses are used. The quaternary Ge–In–Sb–Te alloy based on the Sb–Te eutectic system has been used as the recording layer in phase change optical disks such as rewritable compact disks<sup>1)</sup> (CD-RW), rewritable digital versatile disks<sup>1,2)</sup> (DVD±RW), and digital video recording (DVR) disks<sup>3,4)</sup> throughout.

Recently, nitrogen doping has been adopted to improve the performance of phase change optical disks.<sup>5–7)</sup> Nitrogen atoms in phase change materials exist as interstitial atoms and the nitrides, which cause internal residual stresses, may induce the change in the composition of the phase change material. The structure and composition of the phase change material including factors such as bonding state and impurities, affect the direct overwriting,<sup>5)</sup> optical,<sup>6)</sup> microstructure,<sup>7)</sup> thermal and dynamic properties<sup>5–7)</sup> of recording media have been reported. Nevertheless, most nitrogen doping studies have focused on stoichiometric materials such as  $Ge_2Sb_2Te_5$ ,  $Ge_1Sb_4Te_7$  and  $Ge_1Sb_2Te_4$ , while the eutectic Sb–Te system is yet to be explored. In this work, we doped nitrogen in the eutectic Ge–In–Sb–Te recording layer of optical disks and investigated their signal properties and data transfer rate using dynamic tests. Transmission electron microscopy (TEM) was utilized to examine the microstructural changes induced by nitrogen doping, and the effects of the these changes on data transfer rate and/or recrystallization speed are discussed.

### 2. Experimental

Figure 1 illustrates the multilayer structure of the optical disk used in this work. Disk samples were prepared using a

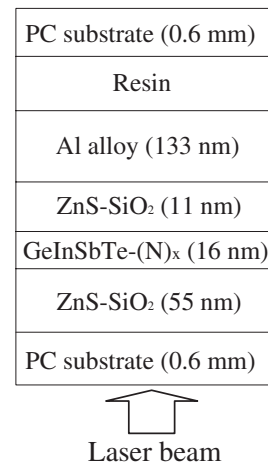


Fig. 1. Cross-sectional structure of optical disk.

SFI (Surface Interface Corp.) sputtering system at a background pressure of  $1 \times 10^{-6}$  Torr. The multilayer structure was deposited on a 0.6-mm-thick polycarbonate (PC) substrate in the sequence ZnS–SiO<sub>2</sub> (55 nm)/GIST-(N)<sub>x</sub> (16 nm)/ZnS–SiO<sub>2</sub> (11 nm)/Al–Cr (133 nm). During the deposition of the recording layer, the  $N_2/Ar$  flow rate was adjusted to values of 0%, 0.5%, 1%, 3%, 5% and 10% to obtain undoped and nitrogen-doped specimens. The sputtering conditions and designated sample numbers are listed in Table I.

After they were initialized under the conditions shown in Table II, the disks were sent to a dynamic tester (DDU1000, PULSTEC Co.) having a pickup head with a 650-nm-laser diode and a 0.6#NA objective lens to evaluate their signal properties. Figure 2 shows the writing strategy used in this study, and Table III presents the measurement conditions. At the beginning of a dynamic test, the disks were written at various laser powers (7 to 15 mW) with fixed erasing power ( $P_e = 6$  mW) and reading power ( $P_r = 0.7$  mW) at various linear velocities to identify the appropriate writing power ( $P_w$ ). Then the track recorded with 8T signals was erased by irradiating a DC laser beam of various laser powers (3 to

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Table I. Sputtering conditions and sample numbers.

Sample no.	N <sub>2</sub> flow (sccm)	Ar flow (sccm)	N <sub>2</sub> /Ar ratio	Target material	Sputtering pressure (mTorr)	Sputtering power (W)
	0	10	0	ZnS–SiO <sub>2</sub>	3	250 (RF)
	0	10	0	Al–Cr	3	400 (DC)
N000	0	10	0	GeInSbTe	3	50 (RF)
N005	0.05	10	0.5%	GeInSbTe	3	50 (RF)
N010	0.10	10	1.0%	GeInSbTe	3	50 (RF)
N030	0.30	10	3.0%	GeInSbTe	3	50 (RF)
N050	0.50	10	5.0%	GeInSbTe	3	50 (RF)
N100	1.00	10	10.0%	GeInSbTe	3	50 (RF)

Ge:In:Sb:Te = 4.5:4:65.95:25.55 (wt.%)

Table II. Initialization conditions for optical disks.

Initializing Mode	CLV
Linear velocity	2.0 m/s
Feed per revolution	50 μm/rev
Start position	22 mm
Terminating position	55 mm
Laser power	1000 mW
Servo-on laser power	1500 mW
Minimum A/F offset	–100

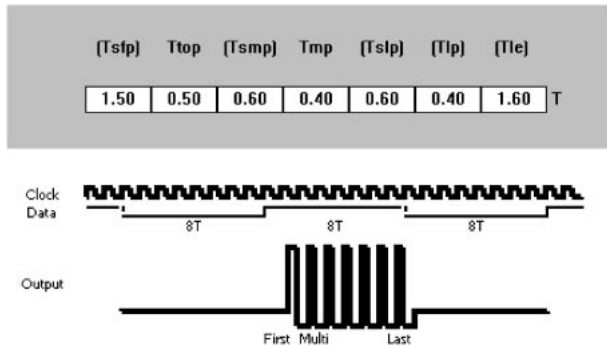


Fig. 2. Writing strategy for 8T signal.

7 mW) at a linear velocity the same as that used for recording. The carrier-to-noise ratio (CNR) was measured before and after erasing to determine the attenuation of the 8T signal carrier, and the value of the attenuation of the 8T signal carrier was defined as the DC erasability.

The method reported by Chen *et al.*<sup>8,9)</sup> was adopted in preparing the plan-view TEM (PTEM) specimens. After removing the PC substrate, the disk sample was cut into small pieces using scissors. A piece of 3M tape was applied to the disk to peel off the Al–Cr reflection layer. After the dissolution of the PC substrate in CH<sub>2</sub>Cl<sub>2</sub> solution, the specimen was mounted on copper mesh and transferred to a TEM (Philips tecnai TEM 20) for microstructure observation.

### 3. Results and Discussion

#### 3.1 Dynamic test

The CNRs and jitter values of the disk samples were measured as functions of  $P_w$  (7 to 15 mW) at linear

Table III. Measurement conditions for optical disks.

Data transfer rate (Mbps)	11.08	16.62	22.16	27.70	33.24
Wavelength (nm)	650				
NA	0.6				
Recording bit length (μm)	0.267				
Modulation method	8/16				
Channel CLK (MHz)	26.16	39.24	52.32	65.4	78.48
Tw (ns)	38.2	25.48	19.09	15.29	12.74
Const. linear velocity (m/s)	3.5	5.3	7.0	8.8	10.5

velocities of 3.5, 5.3, 7.0, 8.8, and 10.5 m/s, as shown in Figs. 3(a)–3(e). It was found that the disks failed the dynamic test when too much nitrogen (N<sub>2</sub>/Ar ≥ 5%) was doped in the recording layer of disks. This was probably because reactive sputtering induced by nitrogen gas might generate deposition defects and hence damage the signal properties of the disks. Figure 3 also shows that, regardless of the amount of nitrogen doping, all the CNRs of the disk samples increase with the increase in  $P_w$  while the jitter value decrease with the increase in  $P_w$ . At approximately  $P_w$  ≥ 12 mW, both CNR and jitter reached saturation beyond which no obvious change was observed with further increases in  $P_w$ .

For all the samples, the CNRs were above 63 dB and the jitter values were below 10% at all linear velocities tested, although a slightly increasing trend was observed in the nitrogen-doped samples. The data from dynamic tests indicated that the variation in the saturated CNR was in fact related to the change in the intrinsic noise level of the disk samples after initialization; the noise level of samples N000, N005, N010 and N030 were –72.71 dBm, –72 dBm, –71.6 dBm and –68 dBm, respectively. The change in the noise level of each sample revealed that the microstructures of all the samples were differed with the level of nitrogen doping in the Ge–In–Sb–Te recording layer.

The method of DVD jitter evaluation was adopted to measure jitter for all intervals between the data and the clock.<sup>10)</sup> A low jitter implies a very low error when 8T marks were written in all disk samples. Furthermore, the threshold power of each sample also increased with increasing linear velocity because the laser irradiation time was shorter at higher linear velocities.

An appropriate  $P_w$  value corresponding to the saturated values of CNR and jitter was chosen to carry out the DC erasability test at various  $P_e$  values (3 to 7 mW). Figure 4 shows the DC erasability of 8T signals as a function of linear velocity and/or data transfer rate at various N<sub>2</sub>/Ar ratios. The output of DC laser power was adjusted so that the DC erasability at each linear velocity reached its maximum value. A DC erasability higher than 25 dB is required for overwriting.<sup>4)</sup> Furthermore, the DC erasability of each disk sample significantly decreased with an increase in linear velocity. This result was attributed to the fact that the laser irradiation time at a high linear velocity is shorter than that at a low linear velocity. Laser irradiation time at a specific linear velocity is expressed as<sup>11)</sup>

$$T = D/V, \quad (1)$$

where  $T$  is the laser irradiation time,  $D$  is the diameter of the laser spot and  $V$  is the linear velocity of the disk.

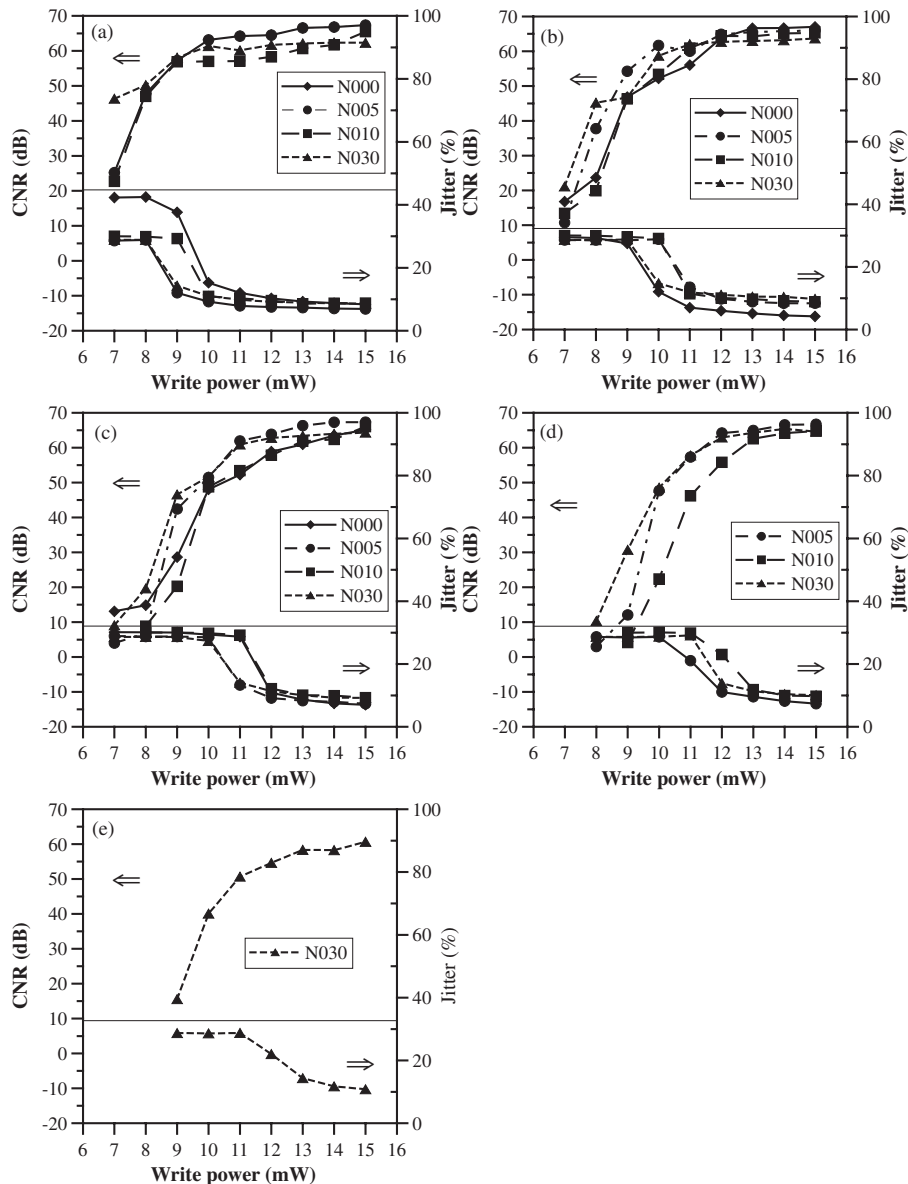


Fig. 3. CNR and jitter of each disk as functions of write power at linear velocities of (a) 3.5 m/s, (b) 5.3 m/s, (c) 7.0 m/s, (d) 8.8 m/s and (e) 10.5 m/s.

Equation (1) indicates that a recording material must possess a sufficiently high recrystallization speed for phase change so that amorphous marks can be effectively erased at a specific linear velocity. Therefore, it is necessary for a phase change optical disk to have a high recrystallization speed to realize a high data transfer rate. From the results of the DC erasability test shown in Fig. 4, disk sample N000 only passes the test requirement at a linear velocity below 5.3 m/s. However, the nitrogen-doped samples, for instance, disk sample N030 sample successfully passes the DC erasability test requirement at a linear velocity of 8.8 m/s. This means that the recrystallization speed of sample N030 was approximately 1.6 times higher than that of the nitrogen-free sample. Apparently, an appropriate amount of nitrogen doping increased the data transfer rate and/or recrystallization speed of Ge-In-Sb-Te phase change optical disks.

Figure 5 shows the jitter values of disk sample N000 and N030 for various direct overwriting cycles. The jitter values of both samples are quite similar for the same number of

direct overwriting cycles. This implies that a relatively small amount of nitrogen doping does not deteriorate signal properties of disks.

### 3.2 TEM Observation

Figure 6 shows the microstructures of samples N000 and N030 initialized under the conditions shown in Table II. The lamellar-like structure commonly seen in a eutectic recording alloy is observed in both samples. In addition to the higher degree of structural irregularity, we observed tiny precipitates uniformly distributed in sample N030 at high magnification. These precipitates are thought to be nitrides, *e.g.*, Ge-N, Sb-N, Te-N and In-N.

The micrographs of the 8T signal of disk samples N000 and N030 written at linear velocities of 7 m/s and 10.5 m/s are shown in Fig. 7. The 8T amorphous marks formed at an optimal  $P_w/P_e$  are depicted in Figs. 7(a) and 7(b). The amorphous marks in sample N000 possess a more distinctive shape than those in sample N030. Probably due to the

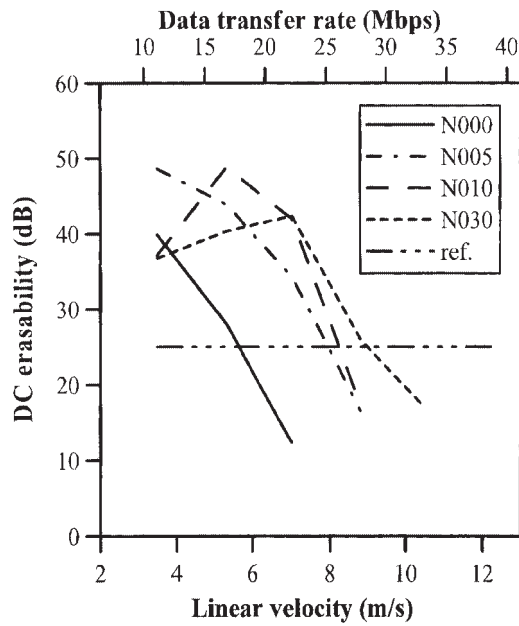


Fig. 4. DC erasability of 8T signals as a function of linear velocity and/or data transfer rate at various N<sub>2</sub>/Ar doping ratios.

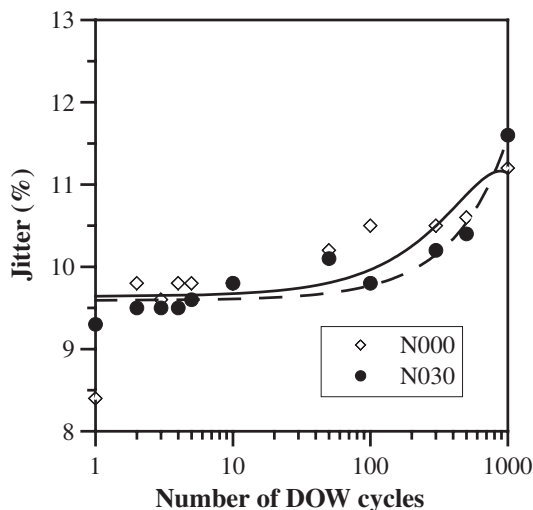


Fig. 5. Jitter VS. number of direct overwriting cycles at 3.5 m/s for samples N000 and N030.

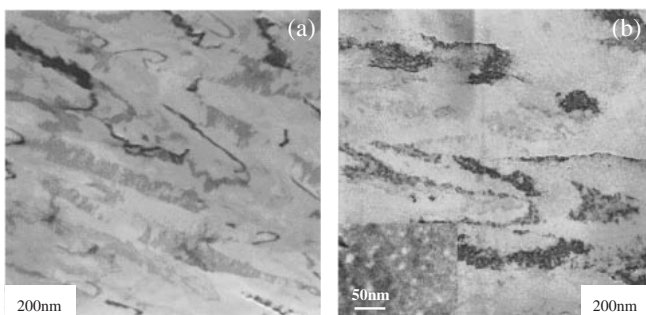


Fig. 6. Microstructure of samples (a) N000 and (b) N030 after initialization. A local magnified picture of (b) is attached at the lower left-hand corner of the micrograph.

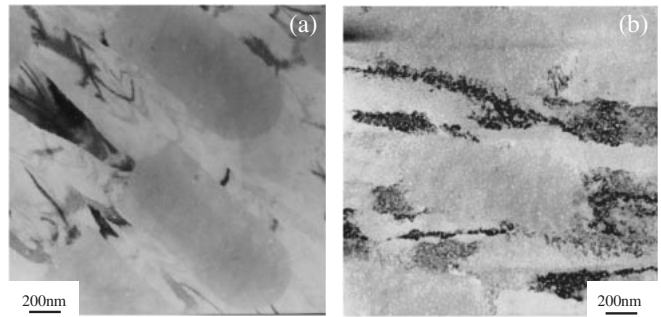


Fig. 7. Micrographs of the 8T signal marks of samples (a) N000 and (b) N030 written at linear velocities of 7 m/s and 10.5 m/s.

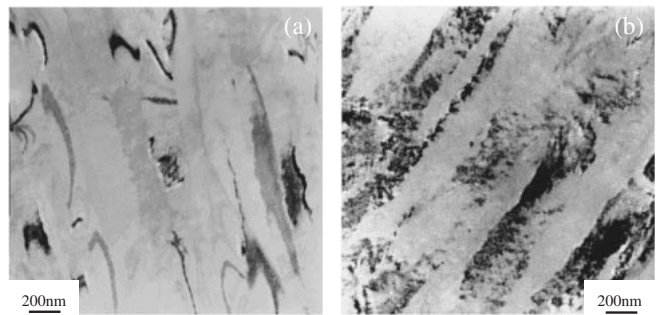


Fig. 8. Micrographs of residual amorphous marks on disk samples (a) N000 erased at linear velocity of 7 m/s and (b) N030 erased at linear velocity of 10.5 m/s.

scattering of the laser beam by precipitates and the indistinct edge of the marks, the noise level of sample N030 is higher than that of sample N000 as observed in the dynamic test. The indistinct marks cause greater discrepancy between data points and the clock as seen in the DDU1000 dynamic tester so that the jitter of sample N030 was higher than that of sample N000, as shown in Fig. 3.

Figure 8 shows the micrographs of the residual marks of samples N000 and N030 separately erased at the linear velocities of 7 m/s and 10.5 m/s. As shown in Fig. 8(a), residual marks can be easily found in the undoped sample, while in the nitrogen-doped specimens residual marks were hardly observed [Fig. 8(b)]. This explains why the DC erasability of an undoped sample is inferior to that of a nitrogen-doped specimen as shown in Fig. 5. The microstructural observation also reveals that the recrystallization behavior of the nitrogen-doped specimens should be different from that of the undoped specimen due to the existence of tiny nitride precipitates.

### 3.3 Recrystallization model

The eutectic Ge–In–Sb–Te alloy is called the fast-growth material because its recrystallization is initiated from the crystalline-amorphous interface and the amorphous mark shrinks as the grain growth propagates toward the center of the mark,<sup>12–15</sup> as illustrated in Fig. 9(a). According to the theory of grain growth, the velocity of grain growth is derived from the net jump frequency of atoms across the amorphous-crystallization interface and can be expressed as<sup>14)</sup>

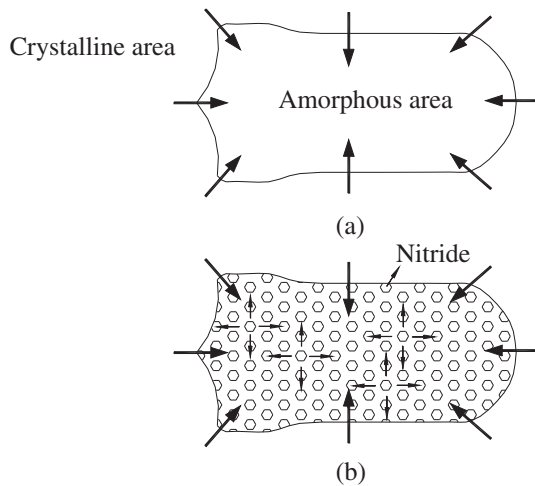


Fig. 9. Schematic illustration of recrystallization of (a) undoped and (b) nitrogen-doped samples.

$$V(T) = V_0 e^{-\frac{E_a}{R\Delta T}} \left( 1 - e^{-\frac{\Delta g^{ac}}{RT}} \right), \quad (2)$$

where  $V_0$  is a pre-exponential factor,  $E_a$  is the activation energy of transition from the amorphous to the crystalline state,  $\Delta g^{ac}$  is the free energy difference between an atom in the amorphous phase and that in the crystalline phase,  $R$  is the gas constant and  $\Delta T$  is the temperature difference between the interface temperature and the glass transition temperature. In our TEM observations, residual marks were hardly observed in the nitrogen-doped samples. According to the recrystallization model shown in Fig. 9(b), nitrogen doping might generate numerous nanometer-scale precipitates uniformly distributed in the GIST recording layer. The amorphous-crystalline edge of marks may also be preferential sites for the amorphous-crystalline transition<sup>12,13</sup> in recording media. The tiny precipitates not only induce heterogeneous nucleation, but also shorten the distance for the grain growth required to complete the transition.

#### 4. Conclusions

We demonstrated that nitrogen doping is a promising method of enhancing the data transfer rate of a Ge–In–Sb–Te phase change optical disk. Nitrogen doping may increase the recrystallization speed of the Ge–In–Sb–Te recording layer which, in turn, enhances the data transfer rate of a disk at high linear velocity. However, according to our dynamic tests, too much nitrogen doping ( $N_2/Ar \geq 5\%$ ) caused disks

to fail the dynamic test. Even though the noise level and jitter of the optical disks were increased slightly by nitrogen doping, the data transfer rate and/or recrystallization speed of the optical disks increased approximately 1.6 times without severely damaging signal jitter when doped at an  $N_2/Ar$  flow ratio of 3%. The TEM observations revealed that nitrogen doping might produce tiny nitride precipitates that are uniformly distributed in the recording layer. These precipitates provide numerous preferred sites for amorphous-crystalline transformation and thereby promote the velocity of recrystallization.

#### Acknowledgement

This work was supported by the Ministry of Education of the Republic of China with the Academic Center of Excellence in “Photonics Science and Technology for Tera Era” under contract No. 89-E-FA06-1-4 and the National Science Foundation, Taiwan, under Grant NSC92-2216-E009-013.

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