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Preparation of nanocomposite for optical application using ZnTe nanoparticles and a zero-birefringence polymer

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Abstract Surface-modified ZnTe nanoparticles were mixed in a zero-birefringence polymer matrix. Transmission electron microscopy images revealed that aggregates of ZnTe nanoparticles with a diameter of ~20 nm were uniformly dispersed in the polymer. The transmittance of ZnTe nanocomposites rapidly decreased at wavelengths shorter than the critical wavelength corresponding to the band gap of ZnTe nanoparticles, an effect which became significant as the volume fraction of particles increased. In this way, the optical characteristic of ZnTe nanoparticles was added to the polymer. The intrinsic zero-birefringence was confirmed in the heat-drawn ZnTe nanocomposites. As the ZnTe nanocomposites were left in air, a lowering of transmittance was observed. This was due to the oxidation of Zn and the resultant deposition of Te in the ZnTe nanocomposite, as the light absorption of Te is significant. The formation of oxygen non-permeable SiO_2 films onto the ZnTe nanocomposite by the sol-gel method was useful in preventing oxidation so that the decrement of transmittance decreased from 47.2% to 14.9% at 530 nm near the ZnTe band gap.

Introduction

Composites constructed by embedding nanoparticles with optical functions into a transparent matrix have attracted much attention in the field of applied optics, namely in applications calling for high-refractive-index materials [1, 2], light-emitting elements [3, 4], optical fibers, optical switches, non-linear optical devices, and optical circuits [5, 6]. In nanocomposites composed of nanoparticles embedded in a transparent polymer matrix, the optical properties of the nanoparticle can be added to the matrix without loss of transmittance, as scattering loss due to nanoparticles with diameters below 20 nm is scarcely expected [6]. When nanoparticles of magnetic materials are used in the nanocomposite, a magneto-optical characteristic is provided to the polymer. Such magnetic nanocomposites are candidates for new magneto-optical materials to take the place of single-crystal materials commercially applied to magneto-optics [7, 8]. Nanocomposites have some advantages in cost because of higher efficiency in the fabrication or manufacturing process compared with single crystalline materials. Furthermore, many kinds of materials can be obtained as nanoparticles without much trouble even if they cannot be prepared in bulk. Thus, we have a large selection of nanoparticle materials. In addition, the magneto-optical properties of nanoparticles can be controlled by the size and dispersion state [6].

For the sake of the fabricating high-quality magnetic nanocomposites, the use of a matrix with negligible birefringence and well-dispersed nanoparticles having a small size distribution and a large magneto-optical effect is essential. The birefringence degrades the performance of magneto optical materials due to the disturbance of the polarization state of the incident light in the polymer. Optical polymers that have high transparency and can be

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mass-produced by injection molding are useful as the matrixes of nanocomposites for magneto-optical applications, because they have several advantages as compared with glasses: e.g., low cost, light weight, easy processing, and easy handling. However, the polymer has orientational birefringence during the melt flowing and cooling stages in the injection molding process. Recently, Iwata et al. [9] prepared a transparent zero-birefringence optical polymer in which the orientational birefringence is eliminated. Therefore, a magnetic nanocomposite composed of the transparent zero-birefringence polymer and magnetic nanoparticles should be a strong candidate for the next generation of magneto-optical materials.

Nanoparticles of ferromagnetic diluted magnetic semiconductors (DMSs) with large magneto-optical effect can be suitably used to prepare transparent magnetic nanocomposites, if they have little optical absorption and are well dispersed in the polymer. $Zn_{1-x}Cr_xTe$, the only DMS showing room-temperature ferromagnetism, was recently synthesized using a molecular beam epitaxy (MBE) [10]. The use of $Zn_{1-x}Cr_xTe$ in nanocomposites is anticipated if it can be obtained in nanoparticle form, although this has not yet been successful. As groundwork for the preparation of $Zn_{1-x}Cr_xTe$ nanocomposites, therefore, we studied a nanocomposite using the II–VI semiconductor ZnTe, whose optical properties are similar to those of $Zn_{1-x}Cr_xTe$ [10].

There has not been any report on magnetic semiconductor nanoparticles dispersed into a zero-birefringence polymer. Aggregations of nanoparticles in polymers are frequently observed because of their high specific surface energies. Thus, much effort is necessary to prepare a transparent nanocomposite with homogeneously dispersed nanoparticles in the polymer matrix [11, 12], and only a small group of materials has been successfully used in such nanocomposite fabrication [13, 14]. Fewer studies have been performed for semiconductor nanoparticle–polymer nanocomposites compared with metal or monoatomic nanoparticle–polymer nanocomposites, and the former type has been insufficiently characterized in terms of the dispersion state of the nanoparticles and the optical properties of the nanocomposite [2–4, 15, 16]. There have been no reports on ZnTe nanocomposites. Therefore, the study of a transparent ZnTe zero-birefringence polymer nanocomposite in which the nanoparticles are uniformly dispersed should become a guide for the study of the very promising $Zn_{1-x}Cr_xTe$ magnetic nanocomposite.

In this article, we show that a ZnTe zero-birefringence optical nanocomposite can be successfully prepared. We describe the optical characteristic of the prepared nanocomposite, which mimics those of a semiconductor having the characteristics of ZnTe nanoparticles. In addition, we propose a method to prevent the oxidation of Zn in ZnTe nanocomposites, which inevitably occurs as the nanocomposite sample is left in air, by means of an SiO_2 coating. The strategies proposed in this article can be applied to the other magnetic or optical composite materials. In fact, the present work was intended as a pilot study to advance technologies for the production of magnetic nanocomposites to be used as magneto-optical materials in the future.

Preparation of ZnTe nanocomposite

Preparation of ZnTe nanoparticles

Surface-modified ZnTe nanoparticles were synthesized based on the hot soap method developed by Murray et al. [17]. In this method, tri-*n*-octylphospine oxide (TOPO) restricts the particles' size to a nanometer scale and encapsulates them so as to obtain free-standing nanoparticles. Therefore, dispersion of nanoparticles into the polymer is easily realized. The following preparation method was used to prepare the ZnTe nanoparticles.

TOPO (25 g) was heated to about 210 °C in a nitrogen atmosphere. The mixture of diethylzinc (0.69 mL) and TOPTe, in which Te (0.64 g) was dissolved in tri-*n*-octylphospine (TOP) (12.5 mL) in a nitrogen atmosphere, was quickly injected into the bath of TOPO and mixed well by stirring. The reacted solution was heated and kept at 210 °C and refluxed for 30 min. After cooling to room temperature, the particles were precipitated by the addition of ethanol (20 mL) to the reacted solution (10 mL), followed by centrifuging. Tetrahydrofuran (THF) was added to the precipitation and the centrifugal separation was performed; then, the supernatant fluid liquid was used as the ZnTe solution. A yellow or orange solution was obtained at this time.

Figure 1 shows Transmission Electron Microscope (TEM) images of the surface-modified ZnTe nanoparticles and their size distribution, where the sample for TEM observation was prepared by depositing a drop of ZnTe nanoparticless dispersed in THF on a Cu grid. The ZnTe nanoparticles formed agglomerates with sizes ranging from 9 to 31 nm. Each ZnTe nanoparticle had a spherical shape. The size distributions of agglomerates and nanoparticles were Gaussian with average diameters of 14.6 and 5.9 nm, and standard deviations of 5.0 and 1.4 nm, respectively. Lattice images of the prepared ZnTe nanoparticles were obtained in the TEM observation.

The atomic-ratio composition of the prepared ZnTe nanoparticles by the hot soap method was evaluated as Zn:Te = 50.3:49.7 using electron probe microanalysis (EPMA). Figure 2 shows the X-ray diffraction (XRD)

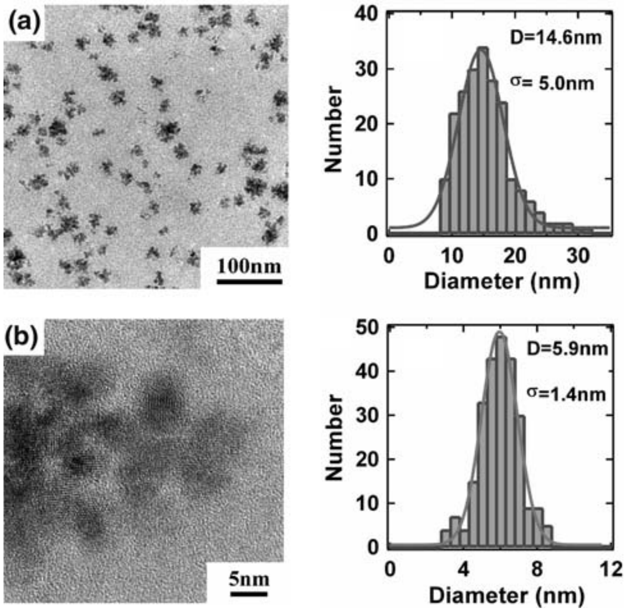


Fig. 1 TEM images and size distributions of ZnTe agglomerates (**a**) and nanoparticles (**b**). (b) is the higher magnification picture for (**a**)

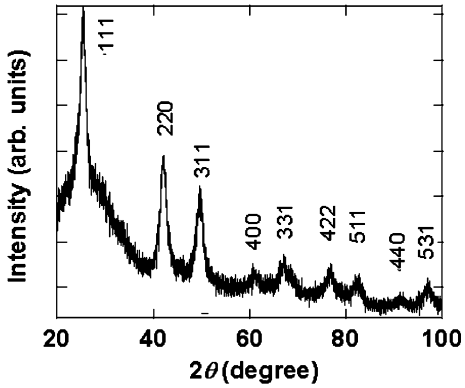


Fig. 2 X-ray diffraction patterns of surface-modified ZnTe nanoparticles

pattern of the sample. All the peaks are assigned to the lattice plane of the zinc-blend structure of ZnTe. The lattice constant of the ZnTe nanoparticles is 6.09 Å, which is comparable to 6.10 Å of the bulk ZnTe. The prepared samples were kept in a nitrogen atmosphere so as to prevent oxidation.

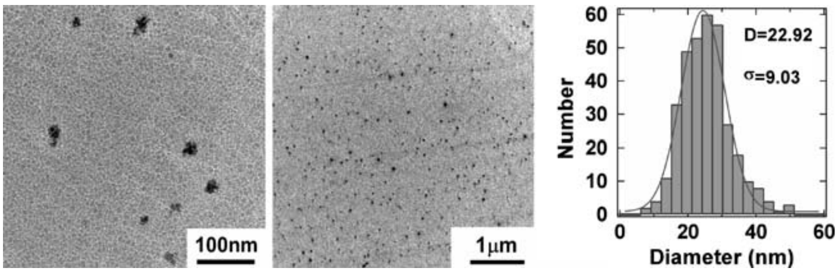
Dispersion of ZnTe nanoparticles into the polymer

The zero-birefringence for any orientation degree of polymer chains, were prepared by the random copolymerization method [9]. We selected methyl methacrylate (MMA) and benzyl methacrylate (BzMA) as monomers. A mixture of MMA (82 wt.%), BzMA (18 wt.%), and benzoyl peroxide (0.5 wt.%) as an initiator and n-butyl mercaptan (0.2 wt.%) as a chain transfer agent was added in a glass tube. The polymerization was carried out at 70 °C for 1 day, yielding poly (MMA-co-BzMA) with MMA:BzMA = 82:18 in weight ratio. Heat treatment of the obtained bulk polymer was performed at 90 °C for 1 day to finalize the polymerization. Then, the resultant bulk was dissolved in acetone. The polymer solution was filtered using a 0.2 μm membrane filter and dropped into methanol so as to precipitate the polymer and remove the remaining monomers. After drying under reduced pressure at 90 °C for 2 days, polymer flakes were obtained.

We prepared the ZnTe nanocomposites with reference to the previously described birefringent crystal dopant method [18, 19]. The zero-birefringence polymer was dissolved in THF with the ZnTe solution, and the polymer solution was spread onto a glass plate using a knife coater to prepare the film samples with a thickness of ~30 μm. These films were dried for 1 day at room temperature, then for 1 day at 90 °C under reduced pressure to eliminate the solvent.

Figure 3 shows the TEM images and the size distribution of the ZnTe nanoparticles in the prepared ZnTe zero-birefringence polymer nanocomposite, where the samples for TEM observation were prepared by cutting the nanocomposite into thin slices with a thickness of 50 nm using an ultramicrotome. Aggregates of 5–50 nm, which were comparable in size to the aggregates of the prepared ZnTe nanoparticles, were observed. Importantly, the size of aggregates was significantly smaller than the wavelength of visible light. Aggregates of surface-modified ZnTe nanoparticles with an average diameter of ~23 nm were uniformly dispersed in the polymer at a rate of one nanoparticle to 8.5×10^{-21} m^3 polymer, for a nanoparticle

Fig. 3 TEM images of ZnTe nanoparticles in the polymer matrix (0.60 vol.%)



volume of 0.60 vol.%. Samples with nanoparticle volumes of 0.26, 0.84, and 1.05 vol.% were also prepared. Their weight fractions, estimated using densities of ρ_{org} = 1.1 g/cm^3 for the organic component and ρ_{ZnTe} = 5.63 g/cm^3 for the cubic ZnTe crystals, corresponded to 1.3–5.4 wt.% under the assumption that the densities of the polymer matrix and the surface modified agent are equal. Thus, we successfully prepared a ZnTe nanocomposite in which the ZnTe nanoparticles were uniformly dispersed in the polymer without any significant aggregation; their particle sizes were maintained during the preparation process.

Evaluation of the ZnTe nanocomposite

Optical properties of ZnTe nanocomposite

Figure 4 shows the ultraviolet–visible (UV–vis) transmittance spectra of the polymer matrix and the ZnTe nanocomposites (sample thickness: 0.03 mm). The transmittance was measured using a spectrophotometer (U-2001, Hitachi instruments service Co., Ltd.). The nanocomposites exhibit good transparency (>80%) at the wavelengths λ longer than the critical wavelength λ_c corresponding to the band gap of ZnTe; the transmittance rapidly decreased in the shorter wavelength range. This is because the light was significantly absorbed only at $\lambda < \lambda_c$. The value of λ_c was evaluated as ~530 nm (=2.34 eV), although the band gap of a ZnTe thin film corresponds to λ = 549 nm (=2.26 eV). This blue shift in the absorption spectrum is expected from the average particle size of ~23 nm, because of the spread of the band gap of ZnTe according to the quantum size effect.

Figure 5 shows the light loss of nanocomposites as a function of the volume fraction, where the light loss is calculated by subtracting the transmittance of the nanocomposite from that of the polymer matrix based on Fig. 4. Thus, the light loss due to the addition of particles is exclusively exhibited in Fig. 5 without contribution from the optical reflection and absorption by the polymer. The light loss increases with increasing ZnTe content, and shows an obvious difference between 400 nm ($\lambda < \lambda_c$) and 700 nm ($\lambda > \lambda_c$). This is caused by the light absorption of nanoparticles. This linear relation between the light loss and volume fraction clearly demonstrates that the optical characteristics of ZnTe nanoparticles were added to the polymer [6].

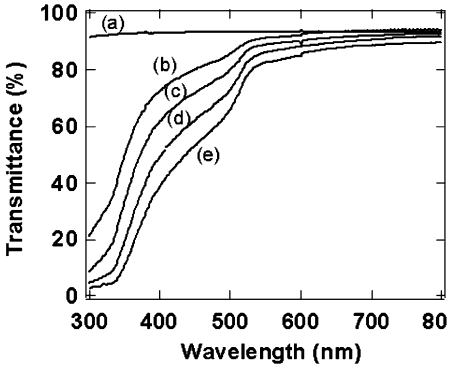


Fig. 4 UV–vis transmittance spectra of the polymer matrix (**a**), and nanocomposites with ZnTe contents of 0.28 vol.% (**b**), 0.60 vol.% (**c**), 0.84 vol.% (**d**), 1.05 vol.%, and (**e**) (sample thickness: 0.03 mm)

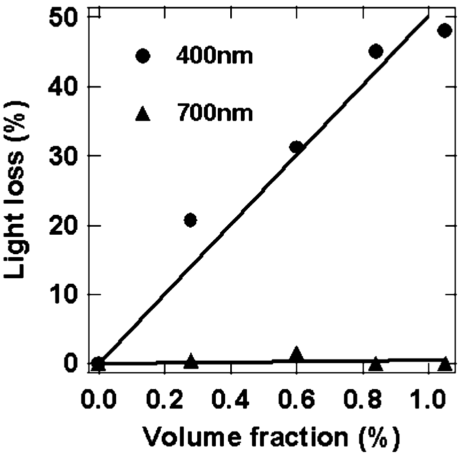


Fig. 5 Relation between volume fraction and light loss of nanocomposites at wavelengths of 400 and 700 nm

Measurements of the birefringence of ZnTe nanocomposite film

In polymer films uniaxially heat-drawn above their glass transition temperature (T_g), the orientational birefringence Δn is defined as $\Delta n = n_{//} - n_{\perp}$, where $n_{//}$ and $n_{\perp}$ are the refractive indices for the light polarized in the directions parallel and perpendicular, respectively, to the draw direction. The dried ZnTe nanocomposites were uniaxially heat-drawn at a rate of 14 mm/s at 130 °C using a universal tensile testing machine (Tensilon RTC-1210A, A&C Co., Ltd.). The orientational birefringence Δn of the ZnTe nanocomposite was measured at a wavelength of 633 nm by optical heterodyne interferometry using birefringence measurement equipment (ABR-10A, Uniopt Corp., Ltd).

The orientational birefringence Δn of the ZnTe nanocomposites under the draw to double the length of film was 1.0×10^{-4} at the most, even for the sample in this study with the maximum particle content. This suggests that the negligibly small orientational birefringence is maintained irrespective of the addition of ZnTe nanoparticles. Thus, we successfully prepared a ZnTe nanocomposite, which combines the zero birefringence of the polymer and the semiconductor optical characteristics of ZnTe nanoparticles.

Preparation of oxygen non-permeable SiO_2 film

Characteristic of ZnTe nanoparticles

Figure 6 shows the XRD patterns of ZnTe nanoparticles kept in vacuum for 20 days and those left in air for 8 and 30 days. For the former sample, only the peak of cubic ZnTe was observed. For the latter samples, however, an additional peak of hexagonal Te was observed as time proceeds. When the ZnTe film was heated at 300 °C in air, the growth of ZnO and the resultant precipitation of Te were observed [20]. Also in the present experiment, the precipitation of Te should be caused by the decomposition of ZnTe to ZnO and Te, although ZnO was not detected in the XRD patterns because it may become amorphous. Namely, ZnTe nanoparticles are easily oxidized in air without heat treatment because they have a large surface area compared with the film sample. To suppress the oxidation of ZnTe nanoparticles prepared by the hot soap method, therefore, they should be dispersed in the polymer just after preparation under a dry nitrogen atmosphere. Furthermore, it is necessary to lower the permeability to oxygen of the polymer matrix. Thus, we attempt to layer an oxygen non-permeable SiO_2 film onto the ZnTe nanocomposite by the sol-gel method to prevent oxidation.

Experimental

We prepared an oxygen non-permeable SiO_2 film to cover the ZnTe nanocomposite by a similar method as that used to prepare SiO_2 film on PET films to prevent the penetration of oxygen and humidity [21]. SiO_2 film is transparent, thereby preventing oxygen penetration without lowering the transmittance. Three kinds of silica alkoxides were used to prepare the oxygen non-permeable SiO_2 film. First, the SiO_2 film was prepared using tetraethoxysilane (TEOS), which is a typical silica alkoxide. However, cracks appeared in the film due to the difference of thermal expansion between the nanocomposite and SiO_2 film. Thus, methyltriethoxysilane (MTES) was added into the TEOS solution to prevent the appearance of cracks. The presence of MTES decreased the tensile stress due to the difference of thermal expansion because a part of the Si–O–Si bond was replaced by a Si–CH_3 bond [22]. In addition, the surface sol-gel method was applied to fill the small cavities existing even in the coating film without any cracks, so that the efficiency of oxygen non-permeability was enhanced. We note that ultra-thin SiO_2 film can be prepared by repeating the chemisorption of silica alkoxides and their hydrolysis on the surface of a substrate using the surface sol-gel process [23].

The starting solution for SiO_2 coatings was prepared by mixing TEOS, MTES, and ethanol. Water and hydrochloric acid (HCl) were slowly added to the solution with stirring. The composition TEOS:MTES:ethanol:water:HCl = 0.66:0.33:13.62:11:0.07 (mol) was used. The ZnTe nanocomposite was dipped into the solution and pulled up vertically at 1 mm/s. The SiO_2 film covered the entire surface of the nanocomposite using the dipping method. The films were dried after coatings in air at room temperature and heated for 1 h at 90 °C. In the successive surface sol-gel method, tetramethoxysilane (TMOS) and methanol were used as the silica alkoxide and solvent, respectively. This process consisted of the following five steps: immersing into the TMOS solution for 180 s; rinsing twice in methanol for 180 and 60 s; immersing into water to hydrolyze for 180 s; and rinsing in methanol for 60 s. Finally, the film was dried in air at room temperature and heated for 1 h at 90 °C.

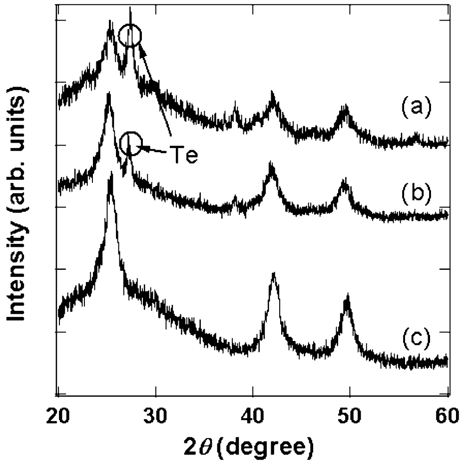


Fig. 6 X-ray diffraction patterns of ZnTe nanoparticles exposed to air for 30 days (**a**) and 8 days (**b**), and those kept in a vacuum for 20 days (**c**)

Evaluation of SiO_2 non-permeable film

Figure 7 shows SEM image of a cross-section of SiO_2 film. The SiO_2 film on ZnTe nanocomposite has a flat surface without any cracks. The film thickness of SiO_2 film, measured by ellipsometer, was ~140 nm. Figure 8 shows the UV–vis transmittance spectra of the ZnTe nanocomposites (0.84 vol.%). A 20–45% decrease in transmittance was observed for the sample left in air for 30 days. The decrease in transmittance was suppressed using the oxygen non-permeable SiO_2 film. This is due to the suppression of oxidation of Zn and the resultant deposition of Te in the ZnTe nanocomposite; otherwise, a decrease in transmittance would occur due to the absorption of light by the semi-metallic Te. We note that the transmittance spectra of the ZnTe nanocomposite coated by SiO_2 showed an obscure change in the vicinity of the ZnTe band gap

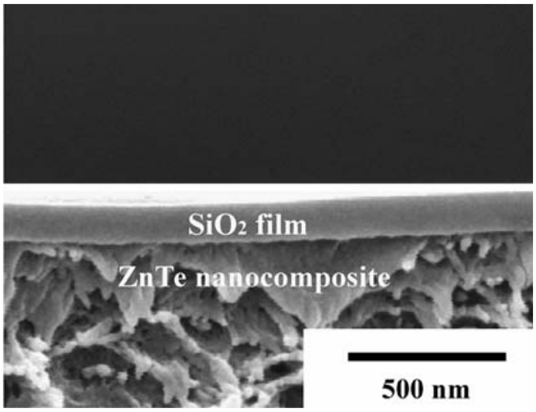


Fig. 7 SEM images of a cross-section of SiO_2 film on the ZnTe nanocomposite

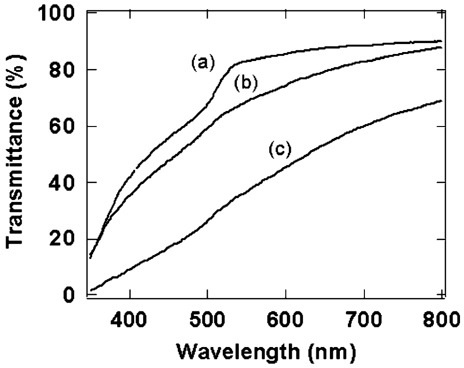


Fig. 8 Transmittance of ZnTe nanocomposite films with thickness of 0.03 mm as a function of wavelength. The data were obtained for a non-coated sample just after preparation (**a**), a SiO_2-coated sample (**b**), and a non-coated sample exposed to air for 30 days

compared with the data taken just after the sample preparation. This is because the SiO_2 coating was performed in air. A clear transition in transmittance spectra should be observed when the SiO_2 coating on the ZnTe nanoparticles is performed in a nitrogen atmosphere.

Conclusion

We successfully prepared surface-modified ZnTe zero-birefringence polymer nanocomposite films in which the ZnTe nanoparticles were uniformly dispersed and the optical characteristic of ZnTe nanoparticles was added to the polymer in proportion to the ZnTe content. The dispersion state of nanoparticles and the optical properties of nanocomposites are characterized in detail. In addition, we devised a useful method to prevent the oxidation of Zn in ZnTe nanocomposites. The strategies used in the present work can be applied not only to magneto-optical materials based on ZnTe but also to other nanocomposite systems and optical materials. The present findings will hopefully direct attention in the optical material research community to nanocomposite systems and magneto-optical materials.

References

1. Papadimitrakopoulos F, Wisniecki P, Bhagwagar DE (1997) Chem Mater 9:928
2. Lu C, Guan C, Liu Y, Cheng Y, Yang B (2005) Chem Mater 17:448
3. Firth AV, Haggata SW, Khanna PK, Williams SJ, Allen JW, Magennis SW, Ifor Samuel DW, Cole-Hamilton DJ (2004) J Lumin 109:163
4. Luccio TD, Laera AM, Tapfer L, Kempter S, Kraus R, Nickel B (2006) J Phys Chem B 110:12603
5. Beecroft LL, Ober CK (1997) Chem Mater 9:1302
6. Caseri W (2000) Macromol Rapid Commun 21:705
7. Barnakov YA, Scott BL, Golub V, Kelly L, Reddy V, Stokes KL (2004) J Phys Chem Solids 65:1005
8. Gass J, Poddar P, Almand J, Srinath S, Srikanth H (2006) Adv Funct Mater 16:71
9. Iwata S, Tsukahara H, Nihei E, Koike Y (1997) J Appl Opt 36:4549
10. Saito H, Zayets V, Yamagata S, Ando K (2003) Phys Rev Lett 90:20
11. Kim TY, Yamazaki Y, Hirano T (2004) Phys Stat Sol (b) 241:1601
12. Barnakov YA, Scott BL, Golub V, Kelly L, Reddy V, Stokes KL (2004) J Phys Chem Solids 65:1005
13. Wang TC, Rubner MF, Cohen RE (2002) Langmuir 18:3370
14. Horikawa A, Yamaguchi K, Inoue M, Fujii T, Arai K (1996) Mater Sci Eng A 217/218:348
15. Yiyun C, Pingsheng H, Dazhu C, Ronghui C (2005) J Compos Mater 39:19
16. Lu BC, Cheng Y, Liu Y, Liu F, Yang B (2006) Adv Mater 18:1188
17. Murray CB, Norris DJ, Bawendi MG (1993) J Am Chem Soc 115:8706
18. Ohkita H, Tagaya A, Koike Y (2004) Macromolecules 37:8342
19. Tagaya A, Ohkita H, Mukoh M, Sakaguchi R, Koike Y (2003) Science 301:812
20. Kaito C, Nakamura N, Saito Y (1985) Appl Surf Sci 22:604
21. Mitsui T, Shiratori S (2003) Mater. Res Soc Jpn 28:1211
22. Tadanaga K, Iwashita K, Minami T (1996) Sol-Gel Sci Technol 6:107
23. Maehara Y, Takenaka S, Shimizu K, Yoshikawa M, Shiratori S (2003) Thin Solid Films 65:438