Microstructure and mechanical properties of a ZnS–SiO_2 composite prepared by ball-milling and spark plasma sintering

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ABSTRACT

Raw ZnS and ZnS–SiO_2 powders mixed by a 3-D mixer or by using high energy ball-milling with attritor mixing were successfully densified by spark plasma sintering. The mechanical properties of the sintered part were evaluated in terms of microhardness and fracture toughness and then correlated to the observed microstructure. Because of a finer and more homogeneous microstructure, the mechanical properties of the ZnS–SiO_2 composite prepared from the ball-milled powder showed the best properties among those investigated. Due to the effect of dispersion hardening and crack deflection by the second phase of fine SiO_2, the hardness and fracture toughness were 3.031 GPa and 1.014 MPa·$m^{0.5}$, respectively.

1. Introduction

Phase change-type optical recording media are comprised of either a tellurium (Te) or antimony (Sb) alloy recording layer, which is protected by a ZnS–SiO_2 thin film [1]. Optical recording media have been used for rewritable optical disks such as rewritable compact disks (CD-RW) [2], random access memory digital video disks (DVD-RAM) [3,4], and rewritable DVDs (DVD-RW) [5]. The ZnS–SiO_2 protecting layer enhances the absorption rate of the laser beam on the recording layer, increases the magnitude of the reproduction signal by enhancing the reflective index between the crystal and amorphous phases, and protects the polycarbonate substrate from thermal degradation [6]. The conventional method for depositing a ZnS–SiO_2 protective layer is radio frequency (RF) sputtering. Direct current (DC) cannot be used due to the high electric resistance of the material.

In recent years, it has been necessary to increase the deposition rate to improve thin film productivity. The high sputtering power required for higher deposition rates often causes crack formation within the target, which then shortens the durability of the sputtering target. It is necessary that the sintered target material should have high crack resistance, excellent strength and a homogeneous microstructure. In particular, the sintered target material must have a small number of internal pores and a high relative density. When sputtering is performed using a sintered target of large porosity, a small portion of air which is trapped in the pores can be released. This release increases the difficulty of maintaining a high vacuum level during sputtering [6]. In this study, a ZnS–SiO_2 target was densified by the spark plasma sintering (SPS) process, which is the most effective densification method for hard-to-sinter materials in a short time, because it is difficult to obtain dense ZnS–SiO_2 using conventional sintering [7,8]. After

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sintering, the Vickers hardness and fracture toughness were measured by the indentation fracture (IF) method.

2. Experimental Procedure

Table 1 lists the details of the raw powders. Three types of powders were prepared for the experiments: raw ZnS powder, ZnS–SiO_2 mixed at 62 rpm for 10 h with a 3-D mixer in an Ar atmosphere, and ZnS–SiO_2 that was ball-milled at high energy at 400 rpm for up to 10 h with an attritor. A final composition of ZnS (80 mol%)–SiO_2 (20 mol%), was obtained by weighing and mixing the appropriate amounts of ZnS and SiO_2 powders. At this point, the weights of the ZnS and SiO_2 powders were about 52 g and 8 g, respectively. The jar (2 L) and balls (5 mm) for milling by the high energy ball-milling method were alumina and zirconia, respectively. The ball to powder ratio was 16:1 and ethyl alcohol was used as a ball-milling agent. The ball-milled powder was dried in an oven at 60 °C for 24 h.

SPS was performed with a heating rate of 100 °C/min at various temperatures and pressures in a vacuum atmosphere. The die and punch material was made of graphite with a 20 mm diameter. Densities of the sintered ZnS and ZnS–SiO_2 composite were calculated by utilizing Archimedes' principle. Hardness tests were performed using an HM-123 (Akashi Corporation, Japan) microhardness tester equipped with a 9.8 N load. Each hardness value was calculated from an average of at least twenty indentations. Fracture toughness was measured by the IF method, using the equation given by Niihara et al. [9,10]. The microstructures of the sintered samples were examined with an optical microscope and X-ray diffractometry (XRD) was used for phase analysis.

3. Results and Discussion

XRD patterns for the (a) raw ZnS powder, (b) mixed ZnS–SiO_2 powder, and (c) ball-milled ZnS–SiO_2 powder are illustrated in Fig. 1. The crystal structure was confirmed by comparison of X-ray diffraction and the JCPDS card. In Fig. 1, it can be seen that the crystal structures of ZnS in (a) raw ZnS powder, (b) ZnS–SiO_2 powder mixed for 10 h, and (c) ZnS–SiO_2 powder ball-milled for 10 h were primarily cubic structures, β-ZnS, having crystal orientations of (111), (220), and (311). The mean crystalline size of the (a) raw ZnS powder calculated by the Hall–Williamson method was approximately 40 nm. After ball-milling for 10 h (c), the mean crystalline size was 20 nm. In the case of the (b) ZnS–SiO_2 powder mixed for 10 h, grain size refinement was not observed because the powder was prepared by a simple mixing process (3-D mixer). Therefore, the mean crystalline size of the sample (b) was the same as that of the (a) ZnS raw powder.

Table 1 – Raw powder properties

	ZnS	SiO_2
Mean particle size	5 μm	10 μm
Particle shape	Spherical	Irregular
Purity	99.99%	98%
Vendor	CERAC, USA	STREM CHEMICALS, USA

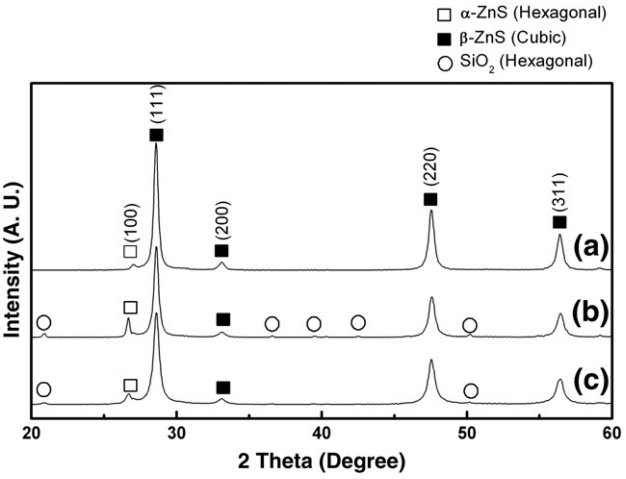

Fig. 1 – XRD patterns of (a) raw ZnS powder, (b) ZnS–SiO_2 powders mixed for 10 h, and (c) ZnS–SiO_2 powder ball-milled for 10 h.

Three types of powders were densified by SPS. Fig. 2 shows the relative densities of the raw ZnS, mixed, and ball-milled ZnS–SiO_2 powder under various SPS conditions. The relative density of the raw ZnS powder increased with increasing sintering temperature. ZnS was fully densified under sintering conditions of 30 MPa at 900 °C for 5 min that becomes 99.47% of the theoretical density. Similarly, the relative density of the mixed ZnS–SiO_2 increased with increasing sintering temperature. However, the sintered density of the mixed ZnS–SiO_2 powder was 87.75%, which was lower than that of the ZnS under the same conditions. It is believed that the presence of SiO_2 makes it difficult to densify mixed ZnS–SiO_2 powders. To obtain the full density, a higher sintering temperature and a higher pressure was applied to the mixed ZnS–SiO_2 powder. The mixed ZnS–SiO_2 powder was fully densified to 99.48% under sintering conditions of 80 MPa and 1100 °C for 5 min. Also, the finer SiO_2 made it difficult to densify the ball-milled ZnS–SiO_2 powder, thus, a higher sintering temperature and

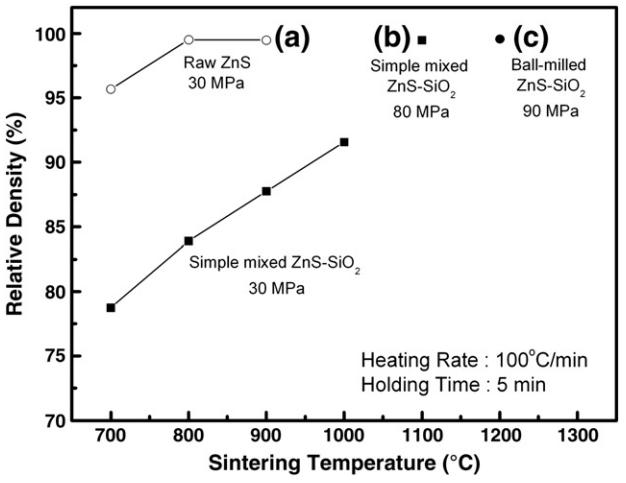

Fig. 2 – Sintered density of raw ZnS, mixed, and ball-milled ZnS–SiO_2 powders under various SPS conditions.