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Magnetic and Microstructural Studies on PVA/Co Nanocomposite Prepared by Ion Beam Sputtering Technique

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ABSTRACT

In this paper, we report the embedment of Cobalt (*Co*) nanoparticles by ion beam sputtering (IBS) in poly(vinyl alcohol) (PVA) substrate to prepare nanocomposite film. The *Co* film of 5 nm was deposited on PVA by IBS technique. Formation of nanocrystalline *Co* with hcp phase is revealed in GIXRD pattern of the film which also indicates that there is no change in the crystalline structure of PVA even after sputtering of the metallic nanoparticles. The average particle size of *Co* nanoparticles as evaluated using Scherer formula is found to be about 2 nm. UV-Vis absorption spectrum of the film showed SPR peaks of *Co* metal in their nano size level embedded in the PVA matrix system. XPS study confirms the metallic nature of *Co* MOKE studies show that the nanocomposite film is ferromagnetic with $Hc_{||}$ of. 42.8 Oe.

Keywords: Nanocomposites, nanomaterials, vinyl polymer, transition metal, magnetic property

1. INTRODUCTION

Cobalt nanostructures have potential applications in the area of high-density magnetic recording system[1]. One of the attractive features of transition metal cobalt (*Co*) is that it can exhibit ferromagnetic property even if its thickness goes down to the extent of ultra thin level. However, *Co* nanostructures have the disadvantage that they have a tendency to get oxidized and this undesired property aggravates further with the decrease in particle size. Thus, researchers are trying hard to protect such nanostructures from oxidation. One of the methods to generate ferromagnetic properties is to embed *Co* nanostructures into a suitable matrix like polymer[2,3]. Polymers have numerous technical applications because of their many fold advantages like, for example lightness in weight, noncorrosiveness, easy mouldability and amenability towards creation of desired shapes and sizes besides their ability to accommodate guest molecules such as metal nanoparticles. Nanocomposite is considered as a system[3-17] which comprises of two or more constituent materials in which each constituent components not only has significantly different physical or chemical properties but they also remain distinctly separated in the system where at least one of them must remain in its nanoscopic level[3-17]. The definition of nanocomposite material has broadened significantly to encompass a large variety of systems including systems where nanoparticles are embedded[13] in the matrix system[3-17]. Therefore metal nanoparticles embedded in polymer matrix leads to the formation of metal-polymer nanocomposite

Poly (vinyl alcohol) PVA is a polymer, which is gaining increasing importance due to its nontoxic nature, easy processability, good film forming ability, biocompability and biodegradability.

This urged us to select PVA as matrix material to accommodate metal nanoparticles for the preparation of nanocomposite system.

Cobalt nanoparticles can be synthesized by various chemical routes as well as physical methods; and such metal particles can be deposited on 2D substrate. However, for magnetic recording purpose, the cobalt metal should be available in the form of thin film form. In such case physical deposition method is preferred over the chemical methods. Sputter deposition method commonly known by the name sputtering is a physical technique often used for developing thin films. In the present work, Ion beam sputtering (IBS) technique has been selected as deposition technique because it ensures good adhesion of adatoms.

In the present systems *Co* was embedded into the PVA vinyl polymer film to prepare cobalt metal nanoparticle embedded polymer nanocomposites where *Co* was present in metallic phase to result magnetic property in the nanocomposite films. In this backdrop, we report in the present paper, embedment of *Co* nanoparticles in PVA film by ion beam sputtering (IBS) technique to prepare nanocomposites. It is worth noting that unlike PVA/Co/C[2] and PVA/Co/Ag[3] nanocomposite systems, no additional over layer was required to generate magnetic property. The structural and magnetic properties of this PVA/Co nanocomposite are described here.

2. EXPERIMENTAL

Prior to deposition, float glass substrate was cleaned ultrasonically. PVA (Mol. Wt. 72 kDa, E. Merk, Germany) was

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dissolved in double distilled water at 60 °C with continuous stirring on a magnetic stirrer. After obtaining clear solution, film of PVA was deposited by solution casting method. A 5 nm layer of *Co* nanoparticles was deposited in PVA film by ion beam sputtering method using Kaufman gun maintaining a base vacuum of ~1×10^{-6} Torr. The Grazing incidence x-ray diffraction (GIXRD) patterns of the samples were recorded on Bruker D8 advanced diffractometer using *Cu* Kα radiation.

Atomic force microscopic (AFM) images were recorded by Nanoscope E digital instrument in contact mode.

XPS was recorded by VSW using *Al* Kα radiation with an overall energy resolution of ~0.9 eV. XPS peaks were fitted using XPSpeak 4.1 software. The magnetization behavior was observed by using Magnetic optical Kerr effect, MOKE method involving He-Ne laser with λ=6328 Å. All measurements were done *ex-situ*.

3. RESULTS AND DISCUSSION

3.1 GIXRD Study

GIXRD pattern of freshly deposited sample of PVA/Co nanocomposite is shown in Fig. 1. The prominent peak at 2θ =19.7° is attributed to PVA, the corresponding interplanar distance is found to be 0.45 nm which agrees well with the reports of the earlier researchers[18] and the small peak at 2θ = 41°, which may be attributed to (100) plane of hexagonal closed pack (hcp) metallic cobalt. These match well with the earlier reported values[2,3]. The small size of *Co* peak (Fig.1) is typical of cobalt with very small thickness[2,3]. PVA is a semicrystalline polymer comprising both the crystalline zone as well as amorphous zone. As the crystalline peak of PVA remains undisturbed even after sputter deposition of *Co* nanoparticles, understandably *Co* does not interact with the crystalline zone of PVA but rather it might have been influenced by the amorphous zone of PVA probably through its OH groups which possibly facilitates the growth of hcp cobalt in the nanocomposite. PVA is seen not only to facilitate the growth of Co nanostructures but also it protects its metallic phase which indicates that the *Co* nanostructures get embedded in PVA matrix resin which

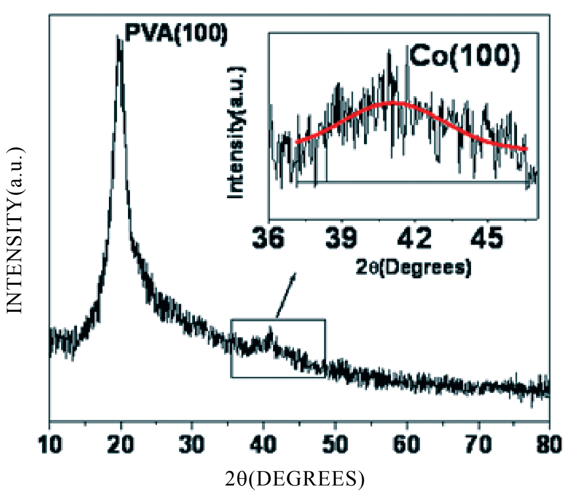

Figure 1. GIXRD pattern of PVA/Co nanocomposite (freshly deposited sample); the inset shows the fitting of Co (100) peak.

protects it from environmental degradation especially from oxidation. Similar kind of observation was reported[2,3] which supports present view. The particle size of *Co* as calculated from Co (100) plane using Scherrer formula is found to be about 2.1 nm. This shows that Co is present in PVA matrix as nanoparticles.

3.2 UV-Vis Spectroscopic Study

To further confirm the presence of Co nanoparticles in the PVA matrix, UV-VIS spectrum of freestanding PVA/Co film was recorded and is presented in Fig. 2. The absorption spectrum shows a well-defined absorption edge at ca. 250 nm, which indicates semicrystalline behaviour of PVA. This result is in confirmation with our earlier report[3]. The absorption band at 280 nm and a shoulder at 330 nm are also in confirmation with our earlier paper and these bands can be attributed to π-π* transitions due to carbonyl groups remaining in the polymer matrix. PVA does not have any absorption bands beyond 330 nm[3,19]. Metal nanoparticles show surface plasmon resonance peak (SPR) and the position of the peak depends on the metal particles, its size and shape. Taking into account these facts, the absorption band around 361 nm in Fig. 2 can be considered as the indication of the presence of cobalt metal in nanostructure form[3,20]. This UV-VIS spectrum confirms that the film prepared for the present study is a kind of nanocomposite material[4-17] which is composed of Co metal nanoparticles and a non-metallic polymer matrix material, PVA.

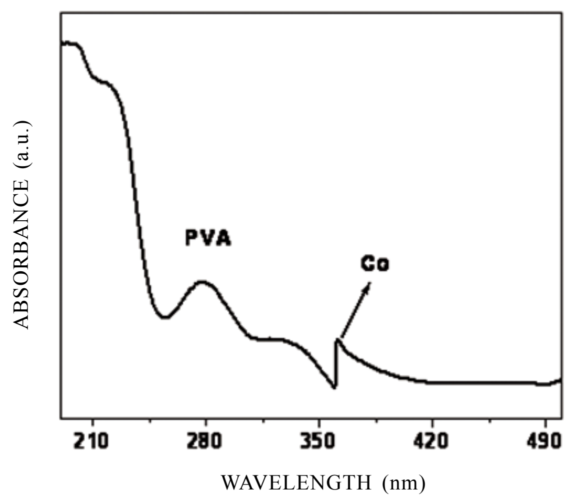

Figure 2. UV-VIS spectrum of freshly deposited PVA/Co freestanding nanocomposite film.

3.3 XPS Study

XPS is a useful technique for investigating the chemical state of an element as also for the depth profiling of the system which means extracting information about the vertical distribution of metal particles embedded in the polymer matrix[3,21]. In the present study, this technique has been used to investigate the chemical state of *Co* nanoparticles as well as the vertical particle distribution in polymer matrix system. The depth profiling analysis of metal embedded in PVA film was carried out by controlling the Ar^+ ion sputtering and *in-situ* XPS measurements.

XPS survey scan of the as deposited (unetched) sample showed prominently C 1s and O 1s peaks. The sample was etched using Ar^+ ion sputtering. As the sputtering time was increased, the intensity of *Co* peak increased while the intensity of C 1s and O 1s peaks decreased. After 35 mins of sputtering, the intensity of C 1s and O1s peaks again started decreasing while the intensity of *Co* peaks started increasing. This indicates that *Co* is embedded inside the PVA matrix system.

Narrow scan of *Co* peaks revealed that in the post sputtered spectra, Co is present in metallic phase. Co 3p peak as present in XPS spectra recorded after 80 mins of sputtering is reproduced in Fig. 3. The *Co* 3p spectrum could be fitted well with one peak indicating the presence of only one kind of cobalt which is metallic cobalt. The binding energy of *Co* 3p state as determined from XPS study is found to be 59 eV which matches well with the reported value of cobalt metal[22,23]. This implies that *Co* nanoparticles are embedded in PVA matrix, thus the sample prepared in this investigation is a PVA/Co nanocomposite system.

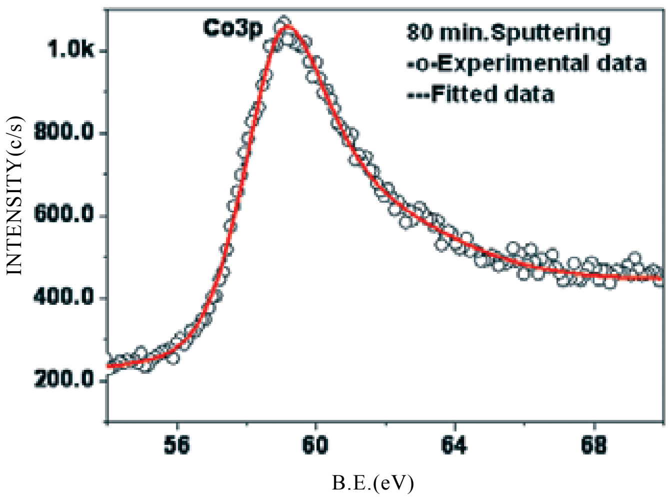

Figure 3. Co 3p core level spectrum of PVA/Co film (freshly deposited) after sputtering of 80 mins; the solid line shows the fitting.

3.4 AFM Study

Surface morphology and surface roughness are important characteristics of a material. AFM image of freshly deposited PVA/Co film is shown in Fig. 4. One can see some discontinuous structures on the surface. These can be attributed to the composite structure of PVA and *Co* nanoparticles. The average size of the composite nanostructures is found to be about 64 nm and the surface roughness is found to be about 5.1 nm. The roughness of bare PVA film as determined from AFM[3] showed a roughness of 2.2 nm. The increase in roughness in case of PVA/Co film can be attributed to the presence of *Co* nanoparticles.

3.5 Magnetic Study

Cobalt is a ferromagnetic material and the distinguishing feature about cobalt is that it can remain ferromagnetic down to ultrathin level. The sample in the present investigation has established itself as a nanocomposite of cobalt and PVA where

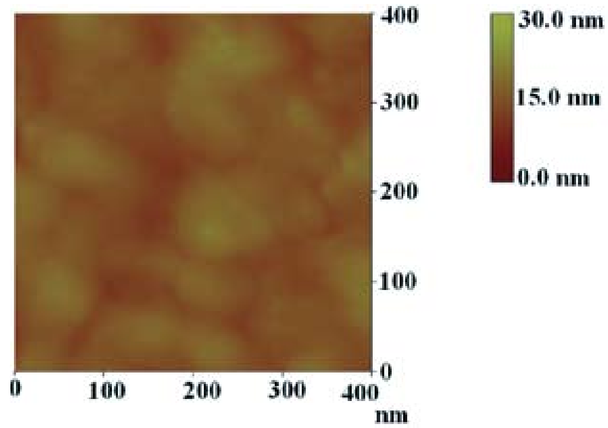

Figure 4. 2D(400 nm x 400 nm) AFM image of PVA/Co nanocomposite film (freshly deposited).

cobalt is embedded in PVA in which Co existing in nanosize level yet retaining its metallic characteristics. It would, therefore, be interesting to study the magnetic behaviour of this polymer/metal nanocomposite film.

The magnetic behaviour of PVA/Co nanocomposite film was studied using MOKE at room temperature. The in-plane magnetic measurements using MOKE are reproduced in Fig. 5. One can see that the sample shows well-defined hysteresis loop with coercivity $Hc_{||}$ of 42.8 Oe indicating soft ferromagnetic behaviour.

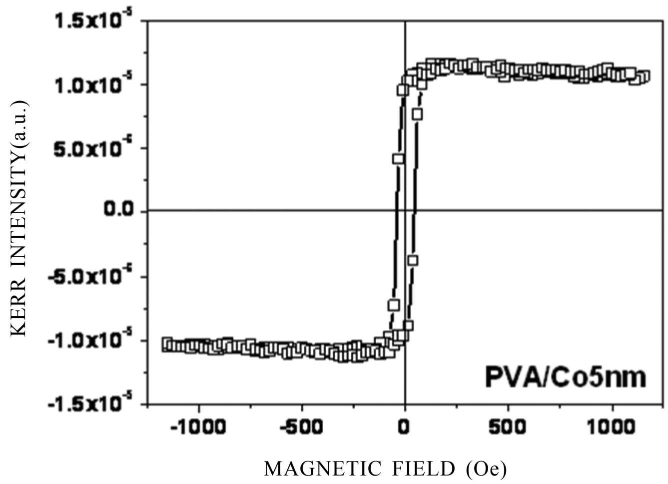

Figure 5. MOKE record of freshly deposited of PVA/Co nanocomposite film.

A comparison of the $Hc_{||}$ value of cobalt films on other substrates reveals that for as deposited 40 nm *Co* film on glass by IBS technique, it is reported to be ~26 Oe[23]; whereas for the as deposited cobalt films on glass as well as Si substrates with the thickness from 50 nm to 120 nm, $Hc_{||}$ is reported to be less than 10 Oe[24]. But here, more importantly, in the present investigation with PVA/Co nanocomposites can bring out better magnetic property.

It is also interesting to note that in earlier publications the authors had reported magnetic study of 5 nm layer of *Co* nanoparticles embedded in PVA matrix having an overlayer of 2 nm of carbon[2] showed ferromagnetic behaviour with a $Hc_{||}$ value of 7 Oe; and in case of 9 nm layer of *Co* nanoparticles in PVA matrix with an overlayer of 4 nm of *Ag* showed corresponding $Hc_{||}$ value of 12 Oe only[3]. Clearly, in this study showed that nanocomposites based on *Co* and PVA without application of the said overcoat is good enough to show that Co can remain protected and give better magnetic properties. Thus PVA/Co nanocomposite is a good candidate for magnetic material.

4. CONCLUSION

It can be seen in this paper that IBS is a good technique for embedding *Co* nanoparticles in vinyl polymer PVA film to prepare magnetic nanocomposite material. PVA provides protection to *Co* against environmental degradation and allows *Co* to remain in metallic state. Besides, PVA is found to act as a good seeding agent allowing the growth of hcp phase of *Co* metal. This hcp phase of *Co* nanoparticles embedded in PVA is responsible for the ferromagnetic behaviour which is found even better than some of the samples deposited on other substrates as reported by other authors.

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