The interaction of light and magnetism in the $\text{Tb}_x\text{Co}_{100-x}$ system

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Abstract

Development of the faster and denser magnetic memory storage elements has been an active area of research since early 20th century. The path of research on magnetization manipulation began with firstly changing the magnetization state of a medium in an external magnetic field, then heating of a medium and magnetizing with a permanent magnet was explored, while the latest efforts have been focused on switching the magnetization only by a polarized laser light. Nowadays due to the technological advancement of lasers and material fabrication methods, the search and development process of magnetic memory elements is much faster. The implementation of such technologies, however, relies on finding suitable magnetic materials which would allow for a fast magnetization writing and read-out processes and would remain magnetized, even with the reduced dimensions. Ferrimagnetic rare Earth - transition metal (RE-TM) alloys have been used for fabricating magneto-optical recording media already since the 1990’s. Relatively recently, in 2007, it was demonstrated that the ferrimagnetic GdFeCo alloy magnetization state can be switched using only circularly polarized laser light. Hence, ferrimagnetic RE-TM alloys could be suitable candidates for all-optical light-induced magnetization switching (AOS), without any external magnetic field. Another combination of RE-TM alloys that was shown to exhibit AOS is ferrimagnetic amorphous alloys containing terbium and cobalt (Tb:Co). They have attracted attention due to their strong out-of-plane magnetic anisotropy, high magneto-optical activity and amorphicity, which makes them attractive from a fabrication point of view since a variety of substrates and buffer layers could be used for growing such layers.

In this Thesis, TbCo alloys are investigated in order to examine how the magnetic, optical and magneto-optical properties could be tuned by varying the elemental ratio and film thickness. The main question that was addressed here was whether such a system is suitable for fabrication of nanosized magnetic elements as the building blocks for the magnetic memory applications. TbCo alloys were prepared as thin films by magnetron co-sputtering method onto different substrates and buffer layers. Films were characterized using a variety of techniques such as an ion beam analysis, an x-ray reflectivity and diffraction, and magneto-optical characterization techniques. It was observed that the properties of such alloys depend not only on the Tb:Co ratio but also on the film thickness and an underlying buffer layer. Magnetization compensation point, at which the magnetization of a film is zero, as in an antiferromagnet, can be modified depending on the buffer layer. All-optical switching (AOS) of magnetization experiments were performed on the fabricated samples. It was determined that AOS with at least 50-100 laser pulses can be achieved for the films grown directly onto fused silica substrates and with the compositions above the magnetization compensation point at room temperature, in the range of 24 - 30 at. % Tb. In the Outlook, the initial efforts of patterning the films into the arrays of nanosized elements are presented. It is demonstrated that after the lithographic patterning of the films, the resulting nanosized elements remained out-of-plane magnetized. In this work it is shown that the ferrimagnetic TbCo alloy system is a potential candidate material for both facilitating AOS and the fabrication of arrays of nanomagnets. Combining the TbCo alloys, which show AOS, together with a suitable buffer layer and patterning the hybrid structure, could enable selective element-by-element magnetization switching for the magnetic memory storage devices.
Skirta mano Mamai, už viską, ką dėl manęs darei,
amžiną atilsi Tėčiui, už tai, kad visada manimi tikėjai...
To my Mother, for everything You have done for me...
To my late Father, for believing in me...
List of papers

This thesis is based on the following papers, which are referred to in the text by their Roman numerals.

I Agne Ciuciulkaitė, Kshiti Mishra, Marcos Moro, Richard Rowan Robinson, Ioan-Augustin Chioar, Bengt Lindgren, Gabriella Andersson, Carl Davies, Alexey Kimel, Andrei Kirilyuk and Vassilios Kapaklis. Design of amorphous $\text{Tb}_x\text{Co}_{1-x}$ alloys for All-Optical Magnetization Switching (Manuscript)

Papers not included in thesis:

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Development of magnetic memory storage devices began in 1956 when IBM developed a first floppy disc containing a magnetic film [1, 2]. The magnetic recording relied on "writing" a magnetic pattern by employing a writing head moving along a continuous semi-hard magnetic layer. Read-out of the recorded data was done by a reading head which would move through the film with a magnetic pattern without affecting it, or in other words, without de-magnetizing it. Usually the reading and writing heads were the same device switchable between these two functions [3]. The magnetic writing by heating, or Curie point magnetic writing, was demonstrated in the 1960’s [4, 5] by heating MnBi, exhibiting an out-of-plane magnetic anisotropy. MnBi was heated above the Curie temperature and a magnetic state was written by drawing a thin permanent magnet wire across the film [4]. In the 1990’s, magnetic memory storage devices based on magneto-optical recording and read-out of data were introduced [6]. Data writing was based on a similar heating principle of a magnetic material as in the previous case of MnBi. A magnetic material now was heated with a laser focused to a micrometer size spot in order to reduce its coercivity. Then it was cooled in an external magnetic field in order to write data by manipulating the magnetic domains. Once the material was cooled, the coercivity would be regained and external magnetic fields would not affect the written data. In such magneto-optical devices the data was read out employing the Kerr effect, where the light polarization and direction of propagation is modified upon reflection from the magnetic domain [6, 7]. The magnetic memory reading and writing relied on the application of the external magnetic fields, and the technologies that were needed for the writing and reading of data as well as a small data storage density, made magnetic memory storage devices costly [2, 6]. Therefore, reduction of magnetic element dimensions and different magnetization writing and read-out processes were needed to increase the magnetic storage density in a device and make it cheaper to be accessible for a wider range of users [2, 6, 8].

Recent advancements in laser technologies and material fabrication tools allow for dimension reduction of elements to be used as a device building blocks. However, a material allowing for a fast manipulation of magnetization, is an essential part of a functional magnetic memory storage device. Rare earth (RE) - transition metal (TM) (TM = Fe, Co, Ni, and RE = Gd, Tb, Ho) amorphous alloys have been a material class of interest (as a candidate) for magneto-optical recording media since the 1990’s [9, 10]. Then nearly all of the magneto-optical devices were manufactured from GdTbFeCo alloys [6].
Compared with ferromagnetic materials, antiferromagnetically coupled systems exhibit fast dynamics [11, 12]. In RE-TM alloys the magnetic moments of both sublattices can be aligned antiferromagnetically to each other due to the exchange interaction between the $f$ and $d$ electrons [10, 13–15]. Tuning the ratio of the two elements, one can reach a magnetization compensation point at which the total magnetic moment approaches zero and the coercivity diverges [9, 10, 16, 17]. Later, in 2007, the magnetization reversal in GdFeCo was demonstrated by Stanciu et al [18] using circularly polarized laser pulses [19] in the range from fs to ps. Since then, a lot of work has been carried out in the area of all-optical switching (AOS) of magnetization where magnetization can be manipulated by light with no external magnetic fields [11, 16, 20, 21].

Other RE-TM alloys, such as TbCo, are also interesting for investigation of AOS. TbCo alloys exhibit a large perpendicular magnetic anisotropy and a high magneto-optical activity compared to the other metallic materials (such as Fe and Ni), and therefore have a potential for incorporation in magnetic memory storage devices [19], where magnetic moments could be switched by a polarized laser light [11, 16, 22]. Furthermore, properties of Tb$_x$Co$_{1-x}$ alloys are easily tunable and films are amorphous when deposited on various substrates.

In this Thesis, a study of preparation parameters and conditions of amorphous RE-TM alloy Tb$_x$Co$_{1-x}$ films are presented. Results of investigations of structural and magnetic properties as well as magneto-optical behaviour, and their dependence on various preparation parameters, are presented. Series of magnetic Tb$_x$Co$_{1-x}$ alloy films with varying Tb:Co ratio and thickness were prepared onto different seeding layers by magnetron sputtering method. It is shown how the structure, magnetic domain size and coercive field as well as magneto-optical response vary in this parameter space. This study shows that Tb$_x$Co$_{1-x}$ is an interesting and versatile material which is easily grown and when sputtered onto amorphous substrates and buffer layers grows as an amorphous layer. Its properties can be easily tuned via variation of atomic composition, thickness and buffer layers. Depending on these parameters, such layers can exhibit AOS of the magnetization and could be used for the fabrication of nanostructured magnetic arrays for magnetic memory elements.
2. Amorphous RE-TM alloys and their characterization

Ferrimagnetic alloys comprised of RE-TM is an interesting class of materials with widely tunable properties and a potential for the magneto-optical data writing and reading [6, 9, 13, 15]. A variety of alloys was investigated since the early 1990’s. GdTbFeCo was already used for magnetization switching in memory reading-writing by a focused laser beam heating [6]. In this Thesis focus is on TbCo alloys since they have a strong perpendicular magnetic anisotropy, large magneto-optical activity and it was demonstrated before that these alloys can exhibit all-optical magnetization switching [11].

Amorphous alloys are attractive from a technological point of view due to the following reasons: (1) it is easy to vary their composition over a wide range without the need of lattice matching in contrast to their crystalline counterparts; (2) no grain boundaries, in contrast to polycrystalline layers [9, 13]; (3) their magnetic properties such as a coercive field, magnetic moment, compensation point $T_{comp}$, Curie temperature, and magnetic anisotropy can be easily tuned by tuning the elemental ratio of the alloy constituent species [6, 9, 15]. These systems exhibit a larger magneto-optical (MO) activity magnitude compared to other magnetic materials such as iron or nickel [9]. However, MO activity decreases with decreasing wavelength of the incident light [2, 6], making magneto-optical activity in small structures very small (since the shorter the wavelength of radiation, the smaller features can be resolved) very small. To enhance MO activity, plasmonic materials, metals such as gold or silver, can be used to fabricate hybrid plasmonic magneto-optically active structures where MO activity in the magnetic material could be enhanced by near-field coupling to the electric field of a plasmonic material [22]. It was shown in various works that combination of a magneto-optically active ferromagnetic material and a plasmonic material in nanosize element arrays could enhance the magneto-optical activity of such a hybrid structure [22–24]. In the Outlook of this Thesis, verification of the suitability of TbCo for the incorporation into magneto-optically active hybrid nanostructures is provided.

2.1 Ferrimagnetic TbCo alloys

The Tb:Co RE-TM system has attracted attention as a candidate for magnetic storage applications due to its ferrimagnetic nature and a strong perpendicular
magnetic anisotropy (PMA) together with high tunable coercivity and square magnetization loops [11, 25]. It was demonstrated that in both alloys and multilayers fabricated from Tb and Co, AOS of the magnetization can be enabled for a range of Tb:Co ratios [11]. In ferrimagnetic Tb$_x$Co$_{1-x}$ a net magnetic moment arises due to uncompensated Tb and Co sub-lattices [9, 16]. For larger RE concentrations, the net moment is pointing along the magnetization of the RE and the net magnetization is called RE-dominant. The same is valid for larger TM concentration, which results in TM-dominant magnetization. Increasing the Tb content, $x$, in a Tb$_x$Co$_{1-x}$ alloy results in an increasing coercive field and decreasing saturation moment of a film since the two sub-lattices become more and more compensated until a certain point at a given temperature, called a magnetization compensation point, $x_{\text{comp}}$ (as indicated in Fig. 2.1) is reached and magnetic moments of both sub-lattices are equal and opposite and cancel each other. Thus the magnetization of an alloy becomes zero [6, 13, 20, 26]. Decreasing the Co content in an alloy even further and going further away from the $x_{\text{comp}}$, the total magnetic moment starts increasing again. Therefore, Tb$_x$Co$_{1-x}$ compositions can be separated into two regions, below and above, the magnetization compensation point, which is varying in both temperature and composition space. That is, there exists not only a magnetization compensation point $x_{\text{comp}}$ at a given temperature, but also a magnetization compensation point in temperature space, $T_{\text{comp}}$, for each given composition, $x$. What is interesting, is that both of the regions exhibit different magnetization dynamic possibilities [11]. It has been reported that in films with compositions below the compensation point the sample is simply demagnetized. On the other hand, in the composition region above the compensation point, magnetization switching can occur via thermally induced incident light-helicity-dependent AOS of magnetization. Since the first find-
ings of AOS in ferrimagnetic alloys, a lot of effort has been spent to find the suitable composition regime for all-optical helicity-dependent switching (AO-HDS) of magnetization for the application in magnetic memory devices [16, 17, 20, 27, 28].

2.2 Magneto-optical effects

Magneto-optical effects manifests themselves when light interacts with a medium and upon such an interaction, the polarization state and propagation direction of light is modified upon reflection off or transmission through that medium [14, 29]. Two types of MO effects can be distinguished. When the material is optically transparent and light is being transmitted through it, the Faraday effect is measured, whereas when light is reflected of a surface of a magnetic material, the Kerr effect is measured. Magneto-Optical Kerr effect (MOKE) can be measured in three different geometries, longitudinal, transverse and polar, depending on the relation between the sample magnetization direction and the light scattering plane (See Fig. 2.2).

![Figure 2.2. Magneto-optical Kerr effect (MOKE) measurement configurations depending on the incident and reflected light (blue arrows) (or the light scattering plane (shaded grey)) with respect to the magnetization direction of the sample (red arrow): (a) longitudinal MOKE (LMOKE) where the in-plane magnetization of the sample is along the light; (b) transverse MOKE (TMOKE) where the in-plane magnetization of the sample is perpendicular to the light scattering plane; and (c) polar MOKE (PMOKE) where the perpendicular magnetization of the sample is in the light scattering plane. $E_{i,p}^s$ and $E_{r,p}^p$ indicate s and ppolarizations of incident and reflected, electric components of light, respectively.](image)

The reflected light intensity is proportional to the sample magnetization and therefore, a magnetization loop is obtained when sweeping the external magnetic field (which is applied along the direction of the sample magnetization). A schematic of a magnetization loop is shown in Fig. 2.3. The polar magneto-optical effect is especially important in magneto-optical data storage since the data is written in the out-of-plane magnetized materials and the written data is read out by detecting changes in the state of the light reflected from a magnetized medium [6, 13, 20]. In this work measurements were performed in the polar MOKE geometry, since the fabricated materials have an out-of-plane easy magnetization axis.
Figure 2.3. Schematics of a characteristic magnetization loop. $M_{\text{sat}}$ indicates the saturation magnetization when a magnetic material is completely magnetized along the field direction. $M_{\text{rem}}$ is the remanent magnetization, i.e. the magnetization when the external magnetic field is zero. $H_c$ is a measure of how strong of an external magnetic field a material can withstand before reaching zero magnetization.

2.3 Optical magnetization switching

All-optical magnetization switching can be observed in ferrimagnetic materials, namely, in alloys and multilayers containing RE-TM, as well as RE-free synthetic ferrimagnets [11, 20]. One such system that was among the first to show AOS is the GdFeCo alloy [28]. Most common means of investigating optical response of these ferrimagnetic systems comprise the use of pump-probe techniques as illustrated in a Fig. 2.4.

Figure 2.4. Schematics of a time-resolved magneto-optical microscopy experimental setup [30]. The CCD camera produces an MO image at a time delay $\Delta t$ after a single pump pulse, using a linearly polarized probe pulse.
The pump pulse is usually a linearly or right- or left- circularly polarized laser pulse with pulse length in the 100 fs range. It is swept across the sample. A probe, the second laser beam, is used for imaging the magnetic structure of the sample. Such an experiment allows investigating magnetization switching behavior depending on the light polarization, and hence, such switching is called helicity-dependent all-optical switching (AO-HDS). It was reported that AO-HDS in RE-TM alloys is possible only when the alloy composition is close to $T_{comp}$. This indicates the importance of heating around $T_{comp}$ for observation of AO-HDS in RE-TM alloys [20]. The broader introduction and discussion of AOS of magnetization are beyond the scope of this Thesis. Instead, this topic is discussed in [11, 12, 17, 20, 26, 31–34].
3. Sample preparation

Amorphous $Tb_xCo_{1-x}$ alloys were prepared via magnetron co-sputtering from elemental Tb and Co targets in the home-built sputtering system Binford. Sample growth via magnetron sputtering using $Ar^+$ ions is schematically shown in Fig. 3.1(a). Magnetron sputtering is a physical vapor deposition (PVD) process in which positively charged gas ions, such as $Ar^+$, are directed by an electric field towards a cathode [35]. The target, which is a material to be sputtered, is placed as a cathode on a magnetron, containing magnets, which confine the plasma near the target for increased process efficiency, arranged as shown in the schematic. Due to the magnetic field lines, the target after sputtering exhibits so-called race tracks. Upon collision of $Ar^+$ ions with the target, its atoms are removed and by following the electric field they are deposited onto a substrate, which acts as an anode.

![Magnetron schematic](image)

Figure 3.1. (a) Schematic of the magnetron sputtering process and a simplified structure of the magnetron; (b) Dependence of Tb content in a $Tb_xCo_{1-x}$ alloy on the power on the Co target.

Alloys containing several different materials can be deposited by co-sputtering from different target materials and the elemental ratio can be varied by changing the power applied on each of the targets. In this work the Tb:Co ratio was varied by keeping a constant power on the Tb target (30 W) and varying the power on the Co target (from 50 to 120 W). The Tb content in the deposited samples was in the range from 15(1) to 37(1) at.% (as confirmed by Rutherford backscattering spectrometry (RBS)). Increasing power on the Co target resulted in the decreasing Tb content in the films and this is shown...
in the Fig. 3.1(b). The base pressure in the system was in the high $10^{-9}$ to the low $10^{-8}$ Torr region. The Ar sputtering gas pressure was 2 mTorr Ar while growing films with Tb content of 15(1) to 24(1) at.% and 3 mTorr growing films with Tb content from 24(1) to 37(1) at.%. Difference in sputtering gas pressure did not result in changed atomic compositions of the films prepared under otherwise the same sputtering conditions within the same growth period. Film composition was confirmed with RBS measurements for separate growth periods one year apart and the results are summarized in the Fig. 3.1(b). The difference in a resulting composition at a given power occurs due to a faster sputtering of Co target due to higher used powers, as well as the changes in system gas pressure. Growth rates of different compositions varied in the range of 1.1(5) to 1.6(5) Å/s.
4. Characterization techniques

4.1 Ion beam analysis

The composition of $Tb_xCo_{1-x}$ alloy films was determined employing ion beam measurements, namely, Rutherford backscattering spectrometry (RBS) and particle induced x-ray emission (PIXE). Both experiments were performed simultaneously, using 2.0 MeV $He^+$ primary ions delivered by the 5-MV NEC-15SDH-2 tandem accelerator at Uppsala University. Schematics of both RBS and PIXE experimental principles are shown in Fig. 4.1(a). An RBS spectrum is obtained by measuring the backscattered particle energy. A typical spectrum shows peaks at the energy values corresponding to the backscattered particles (Fig. 4.1(b)). Samples were loaded on a wheel-sample holder and remotely controlled by a goniometer, which allows for simultaneous data acquisition and sample positioning. A solid state detector (PIPS) with an energy resolution of FWHM $\approx$ 13 keV was placed at the scattering angle $\alpha_{RBS}$ = 170°. The RBS measurements were carried out on a low current and high radiation time regime. The experimental RBS spectra were analysed using the latest version of the SIMNRA code [36, 37].

The composition of films containing two elements, $x$ and $y$, can be determined by solving a two-equation system:

$$\frac{C_x}{C_y} = \frac{I_x}{I_y} \cdot \frac{Z_x}{Z_y};$$ (4.1)

$$C_x + C_y = 1,$$ (4.2)

where $C$ represents respective elemental concentrations, $I$ - represents peak heights, and $Z$ is each element’s atomic number.

As a complementary technique to RBS, Particle Induced x-ray Emission (PIXE) measurements were performed. Similarly to RBS, a material is irradiated with an ion beam with energy in MeV range. Impinging ions ionize the atoms in the sample and electrons from higher energy levels fill the inner shell vacancies. Upon such lower energy level vacancy filling, x-rays characteristic of specific elements are emitted and detected by a detector. PIXE spectra can be recorded simultaneously with RBS spectra. In the experiments performed in this project, spectra were recorded for each sample, by using a silicon drift detector (SDD) with a 79.5 $\mu$m Mylar absorber in front of the Be-window placed at $\theta = 135^\circ$ (resolution: FWHM $\approx$ 143 eV for $Fe-K_\alpha$ characteristic energy).
4.2 X-ray reflectivity and diffraction

Films were characterized employing x-ray scattering techniques: reflectivity (XRR) to determine film thickness and layer roughness, and x-ray diffraction (XRD) to determine whether the material is x-ray amorphous or crystalline [38]. XRR was performed in a Bragg-Brentano geometry where x-ray tube and detector motion is coupled so that $2\omega = 2\theta$ (See Fig. 4.2(a)). Since the samples investigated in this work were thin films, grazing incidence x-ray diffraction (GIXRD) measurements were performed. At the small, or grazing, incidence angles, only the top layers of the structures are probed by x-rays. Performing GIXRD measurements allows identification of the crystallinity of different layers within a structure. In the measurements presented in this Thesis, the grazing angle was varied in the range $\theta = 0.5 - 1.5^\circ$ while the detector was scanning the $2\theta = 10 - 60^\circ$ angle range. Schematics of GIXRD are shown in Fig. 4.2(b).

4.3 Extended x-ray absorption fine structure

A complementary technique to XRD is extended x-ray absorption fine structure (EXAFS) spectroscopy. While XRD probes the atomic plane distances, EXAFS allows probing and quantizing inter-atomic distances. The atomic distances between the nearest neighboring atoms can be resolved and a radial distribution function can be obtained [39–41]. The advantage of EXAFS over
XRD is that it is element specific while XRD provides structural information averaged over all of the different atoms present in the sample [40, 41].

The principle of EXAFS is based on x-ray absorption by atoms. When the energy of an x-ray matches the energy of the core level electron, the x-ray photon is absorbed. Following an electron relaxation to a lower energy level, a photon is emitted and such emitted photons interfere. Upon constructive interference, a peak, while upon destructive interference, a dip is seen in an EXAFS spectrum as illustrated in the schematic shown in a Fig. 4.3. Due to the different energies of the core level electrons in different elements, a broad range of wavelengths, or a continuous energy spectrum and high intensity of x-ray radiation is required [42]. Therefore, EXAFS experiments are avail-
able only in synchrotron facilities. The EXAFS results presented here were obtained in Paul Scherrer Institute, at the SuperXAS beamline.

4.4 Spectral MOKE characterization

Spectral MO measurements, namely, PMOKE and Faraday effect, were carried out as illustrated in Fig. 4.4. Magnetic properties, such as a coercive field, were measured. In the magneto-optical measurements of $Tb_xCo_{1-x}$ alloys, the MO signal is due to Co. When the magnetization of this alloy is transition metal, Co-dominated, the net magnetic moment of the sample points along the Co lattice moment (See Fig. 2.1) and aligns along the direction of an external magnetic field [9, 13]. On the other hand, when the alloy is RE, Tb-dominated, the magnetization points opposite to the direction of the external magnetic field. Therefore, the MO signal measured employing MOKE is of opposite "signs" below and above the compensation point [9]. This can be seen as a reversal of the magnetization loop in MOKE measurements.

![Figure 4.4. Schematics of spectral (a) polar magneto-optical Kerr effect and (b) Faraday effect geometries.](image)

4.5 MOKE microscopy

Due to magnetostatic force, which tries to minimize a system’s total magnetic energy, magnetic domains of various shapes and sizes form within a magnetic material. It is difficult to predict what kind of domains will be formed because the relation of magnetic energy terms can be very complicated. However, the magnetic domain state can be directly imaged employing magneto-optical Kerr effect (MOKE). MOKE microscopy allows imaging the magnetic domains within both ferro- and ferrimagnetic materials by combining an electromagnet with an optical microscope setup [13, 44].

In this work Kerr microscopy was employed in order to investigate a remanent state, that is, the type and size of the magnetic domains at zero field, of the ferrimagnetic TbCo films, prepared on different buffer layers and of different thicknesses. Magnetic nanoelements have to exhibit a single domain state for magnetic memory applications. Therefore, it is important that the
domains in a continuous film are of sufficiently large sizes to be later applicable for patterning into nanosized magnetic elements. Since the films exhibit an out-of-plane magnetic anisotropy, the polar MOKE setup was used with an electromagnet creating a magnetic field perpendicular to the sample surface.

4.5.1 Measurement protocol: Rapid Low Frequency demagnetization

Two types of Kerr microscopy experiments were carried out. First, imaging magnetic domain state at a remanent state. Second, recording magnetization loops and imaging domain reversal.

In order to obtain a remanent magnetic state, films were demagnetized using a Rapid low frequency (RaLF) demagnetization protocol established for demagnetization of soft magnetic out-of-plane magnetized TbCo films. The RaLF protocol was the following: AC field with 10 V amplitude and 5 Hz frequency as a square function and decaying the AC field was applied for a time period in the range of 20-50 s depending on the TbCo film composition. In the beginning of demagnetization, the field was oscillating between +750 and -750 mT and background was subtracted using the Kerr microscope software in the very beginning of the demagnetization while the field was still oscillating with a large amplitude to remove a non-magnetic contribution to the measurement.
4.5.2 Domain size determination by a test line method

According to domain theory, the domain width of a pattern with an arbitrary, not well defined, or regular, structure, could be calculated using a stereological method. That is, drawing a test line (TL) across the investigated area and calculating the number of intersections of the domain walls with that testing line [3]. Then the magnetic domain width (DW) can be calculated using equation 4.3:

\[
DW = \frac{2 \cdot L}{\pi \cdot N},
\]

(4.3)

where \( L \) is the total length of a test line and \( N \) is the number of intersections.

An illustration of this method is shown in Figure 4.6. A limitation to this method is a limited area of investigation. Of course this can be overcome by turning from a manual calculation to an automated computation of the number of times when a pixel along the test line changes its value and normalizing the sum of times to the length of lines as shown in eq. 4.3. However, in the next section a more advanced method based on a similar concept is introduced.

![Figure 4.6. Magnetic domain state at remanence in \( Tb_{18}Co_{82} \) 20 nm thick films prepared on double-side polished fused silica substrate with 3 nm thick Al\(_{80}Zr_{20}\) buffer and cap layers. Investigated area was 584x584 \( \mu m^2 \). The scale bar is 100 \( \mu m \). Black lines indicate testing lines, while orange dots indicate the cross-section between testing lines and domain walls. The domain width calculated using equation 4.3 is \( DW=90.6(469) \) \( \mu m \). The error bar is 50% of the average value, which shows a broad distribution of magnetic domain sizes in this sample. For comparison, determined by the pair correlation function (PCF), \( DW=60.7 \) \( \mu m \) (See Section 4.5.3).](image)
4.5.3 Pair correlation function

Another method for investigation of characteristic domain sizes in a film is application of a pair correlation function (PCF). Using the PCF one can estimate values of pixels in an image with respect to the initial pixel at varying distances from that initial pixel. Using this methodology one can equate the computed nearest neighbor distance to be an average size of a magnetic domain. The PCF is given as

$$ g(r_{i,j}) = \frac{1}{2\pi r dr N} \sum I_{i_0,j_0} \cdot I_{i,j} $$

where $I_{i_0,j_0}$ is the value (between -1 and +1) of an initial chosen pixel in the image, while $I_{i,j}$ is the value of a pixel at a certain distance from the initial pixel $(i_0, j_0)$. The sum is of all the possible pair combinations between the two pixels, over all the possible distances from an initial pixel, while every single pixel becomes an initial pixel while running the script throughout the entire image. The computed intensity was normalized to an area of the two-dimensional shell $2\pi r dr$ and to a number of pixels analysed, $N$. An illustration of PCF for a $Tb_{18}Co_{82}$ sample is shown in Figure 4.7 (b). The domain width (DW) was extracted as the first minimum in the PCF plot. Comparison of TL and PCF methods shows that when the same size area of an image is investigated, both methods are in a better agreement when the domains are of smaller sizes.

Figure 4.7. (a) Magnetic domain state at remanence in $Tb_{18}Co_{82}$ 20 nm thick films prepared on double-side polished fused silica substrate with 5 nm thick AlO$x$ buffer layer and capped with a 3 nm thick, in-situ RF-sputtered AlO$x$ layer. The scale bar is 20 μm; (b) Pair correlation function obtained for the image shown in (a). The average domain size determined by TL method is $DW = 3.29(3)$ μm, while using the PCF, $DW = 3.5$ μm.
4.6 Optical characterization

Since we are interested in the magnetization switching by light, the optical properties of the films are also important. Optical properties of the material can be described by a complex refractive index \( N=n+ik \), where \( n \) is the real part of refractive index, and \( k \) is the imaginary part, or, the extinction coefficient. These parameters can be determined from the ellipsometry measurements, in which the changes in the phase and polarization of the reflected light, \( \phi \) and \( \delta \), respectively, are measured. The \( n \) and \( k \) cannot be directly computed from the ellipsometry data, for this reason a model is required. A detailed description of the ellipsometry technique and the suitable models for using the phase and polarization data for the computation of \( n \) and \( k \) values can be found in [45]. Ellipsometry measurements were performed in the home-built system Apollo using photo-elastic modulator (PEM) and data was fitted using GenX [46] software. The setup Apollo is described in detail in the work by Chioar et al. [47].
5. Results

This Chapter is organized as follows: in Section 5.1 a summary of fabricated samples is provided, in Sections 5.2-5.7 results of ion beam analysis, x-ray scattering experiments, EXAFS measurements, mangeto-optical and ellipso-metric characterization results for the samples prepared on amorphous surfaces, that is, fused silica substrates and Al$_2$O$_3$ and Al$_{80}$Zr$_{20}$ buffer layers, are presented. In Section 5.8 initial results on investigations of Tb$_x$Co$_{1-x}$ films deposited on Au layers are shown.

5.1 Samples

In this section samples which were used for this thesis are summarized. Several different sets were prepared and their structure and composition were varied throughout the period of investigation in order to obtain desired magnetic properties. The buffer layers were varied in order to determine the effect on magnetic properties by the seeding layer. Since the ultimate goal of this PhD project is to fabricate the magneto-optically active plasmonic structures for magnetization switching with light, where metals like Au or Ag are used for their plasmonic magneto-optical activity enhancement effect, the possibility of growth of Tb$_x$Co$_{1-x}$ layers onto a buffer layer of Au was also investigated. Schematics of prepared samples are shown in Fig. 5.1 while exact parameters such as prepared compositions and thickness are summarized in Tables 5.1, 5.2 and 5.3.

<table>
<thead>
<tr>
<th>Table 5.1. AlZr series</th>
<th>Composition, at. %Tb</th>
<th>Tb$<em>x$Co$</em>{1-x}$ film thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>15(1)</td>
<td>20.0(5)</td>
</tr>
<tr>
<td></td>
<td>18(1)</td>
<td>40.0(5)</td>
</tr>
<tr>
<td></td>
<td>22(1)</td>
<td></td>
</tr>
</tbody>
</table>

5.2 RBS and PIXE

In this work, the chemical composition of fabricated films was determined using ion beam analysis methods such as RBS and PIXE. A statistical uncertainty for the Tb:Co ratio presented in Figure 5.2 (a) is found to be $\approx 2$ at.%
Figure 5.1. Structure of samples prepared for this project: (a) AlZr series: an initial batch prepared using Al$_{80}$Zr$_{20}$ as a buffer and capping layer. $x$ represents the content of Tb, which was 15, 18.6 and 22.4 at.% as determined by RBS; (b) Al$_2$O$_3$ series: a series prepared with Al$_2$O$_3$ as a seed and capping layer where the seed layer thickness $t$ was varied from 0 (that is, no seed layer was deposited) to 10 nm for samples with $x=18$; with no seed layer ($t=0$ nm) $x$ was varied from 15 to 34 at.%; (c) Au series: the structure was the same as in (b), except that the films were grown on fused silica substrates coated with Cr(2 nm) and then Au(20 nm)) via electron beam evaporation.

Table 5.2. Al$_2$O$_3$ spacer series

<table>
<thead>
<tr>
<th>Composition, at. %Tb</th>
<th>Sample structure</th>
<th>Al$_2$O$_3$ spacer thickness, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>18.6(1)</td>
<td>Fig.5.1(b)</td>
<td>2.0(5) 5.0(5) 7.5(5) 8.5(5) 10.0(5)</td>
</tr>
<tr>
<td></td>
<td>Fig.5.1(c)</td>
<td>- - - - -</td>
</tr>
</tbody>
</table>

Table 5.3. Composition series, sample structure as shown in Fig.5.1(b) with Al$_2$O$_3$($t=0$), or in other words, no seed layer was pre-deposited

<table>
<thead>
<tr>
<th>Tb$<em>x$Co$</em>{1-x}$ film thickness, nm</th>
<th>Composition, at. % Tb</th>
</tr>
</thead>
<tbody>
<tr>
<td>15(1) 18(1) 22(1) 24(1) 26(1) 28.9(1) 32.5(1) 37(1)</td>
<td></td>
</tr>
<tr>
<td>20.0(5) 30.0(5) 40.0(5)</td>
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<td></td>
</tr>
</tbody>
</table>

whereas systematic uncertainties are estimated to be better than 1%. For the sake of completeness, PIXE spectra were simultaneously recorded for each sample. In Fig. 5.2 (b), a typical PIXE spectrum is shown (see black solid line) with the result from the fit using the GUPIX code [48]. From the PIXE fit, a trace contamination of Cl and Ar (≈0.2 at.%) was found in the sample, while no evidence of heavy trace elements (Z > 11) was detectable in the film (quantification limit > 0.1 at.% for the PIXE measurements in this work). Argon trace-contamination found in the films can be explained by the fact that during Ar$^+$ gas was used for the film deposition.
5.3 XRR and XRD

Measured x-ray reflectograms were used for extracting thickness and interlayer roughness by fitting using the GenX software [46]. An example x-ray reflectogram is shown in Figure 5.3. Comparing two curves representing films with the same composition of Tb$_{15}$Co$_{85}$ and with or without Al$_{80}$Zr$_{20}$ seeding layer, the effect of its presence on film roughness can be directly seen. That is, the identical film prepared onto the seed layer has a smoother interface than one prepared directly on a fused silica substrate. This manifests itself from the higher 2$\theta$ angle at which the Kiessing fringes disappear for the film with the seed layer.

Grazing incidence x-ray diffraction (GIXRD) measurements were carried out as well in order to check possible crystallinity of TbCo films sputtered onto different substrates. This technique allows probing material structure at different depths within the sample and identify origin of the observed reflections. A typical example of a GIXRD diffractogram is shown in Fig. 5.4.

Broad low intensity peaks indicate amorphous layers. In the GIXRD diffractogram a peak associated to an amorphous fused silica substrate can be identified at around 2$\theta$=22°, while no clear peak associated with Tb$_{30}$Co$_{70}$ can be observed.

5.4 EXAFS

XRD and GIXRD measurements showed that the Tb$_x$Co$_{1-x}$ samples are x-ray amorphous due to the absence of sharp high intensity peaks which would indi-
Figure 5.3. Comparison of XRR of two Tb$_{15}$Co$_{85}$ films on glass substrate with Al$_{80}$Zr$_{20}$ seed and cap layers (red) and sputtered directly on a fused silica substrate and capped with Al$_{80}$Zr$_{20}$ (black).

Figure 5.4. GIXRD of a Tb$_{30}$Co$_{70}$ film on a fused silica with Al$_2$O$_3$ cap.

cate crystallinity. To further confirm amorphicity of the samples, EXAFS measurements were performed since it allows determination of a local short range order of atoms within a material. Normalized X-ray absorption spectra obtained for the Tb$_{18}$Co$_{82}$ sample (prepared on a glass substrate) with Al$_{80}$Zr$_{20}$ cap layer is shown in Fig. 5.4. The sample was measured with incident radiation along two perpendicular directions, that is, at a grazing angle, and at a nearly normal incidence, probing in-plane and out-of-plane inter-atomic distances, respectively. For comparison, the spectrum of a crystalline Co film
measured at 80 K temperature [49] is shown. Comparing the absorption spectra one can see that for the oscillations of Tb$_{18}$Co$_{82}$ are of smaller intensity and dissipate at around 8100 eV, while for the crystalline film oscillations are sharp and continues throughout the whole energy range. This is a strong indication that Tb$_{18}$Co$_{82}$ film is amorphous.

![Figure 5.5. EXAFS spectra of the Tb$_{18}$Co$_{82}$ sample deposited on a glass substrate measured at a grazing incidence and at a nearly normal incidence (black and blue lines, respectively). The EXAFS spectrum of a crystalline Co film measured at 80 K is shown as a red line.](image)

5.5 Magneto-optical characterization

5.5.1 PMOKE measurements

Magnetic properties of films were characterized employing Polar Magneto-Optical Kerr effect. Measurements were carried out using the set up shown in Section 4.4. Coercive field dependence on a buffer layer for Tb$_{18}$Co$_{82}$ films of 20 nm thickness is shown in Figure 5.6(a). One can observe that having AlZr as a seed layer results in the highest coercive field as compared to the other buffer layers. AlZr is known as a suitable layer promoting the amorphous growth of metallic magnetic films and providing smooth interfaces [50]. This happens due to reduction of free energy for an amorphous phase in contrast to a crystalline phase [50].

The effect of AlO$_x$ buffer thickness on the coercive field was investigated as well and it is summarized in Fig. 5.6 (b). 20.0(8) nm thick Tb$_{18}$Co$_{82}$ films were fabricated onto a fused silica substrate with an AlO$_x$ buffer layer
of varying thickness (See Table 5.2). Values of the coercive field are similar and after a statistical analysis, the average coercive field value for the whole series of samples is 212.0(438) mT. The initial error bars shown in the plot correspond to the field steps while measuring the magnetization loops. Similar coercive field values were measured for the samples with both Au and varying Al₂O₃ buffer layers (See Table 5.2). The average coercive field value for the samples from Au series was 275(10) mT. The more in-depth study of effects of Au on magneto-optical activity enhancement in TbCo films is out-of-scope of this Thesis and is discussed briefly in the Outlook, since it manifests itself in patterned structures more significantly than in the continuous films.

![Figure 5.6](image)

Figure 5.6. Coercive field \(\mu_0H_c\) dependence of 20 nm thick amorphous \(Tb_{18}Co_{82}\) film grown onto (a) different buffer layers and (b) different \(AlO_x\) thickness.

\(Tb_xCo_{1-x}\) prepared on fused silica substrates

\(Tb_xCo_{1-x}\) films of different thickness, namely, 20, 30 and 40 nm, where \(x\) is the content of Tb in at. % (\(x = 15 - 37\)) were deposited onto fused silica substrates and measured in PMOKE. Resulting coercive field values are summarized in a diagram in Figure 5.7. The shaded area represents a composition range at which the \(Tb_xCo_{1-x}\) film is of compensation composition at room temperature. It can be observed that the coercive field diverges in a narrow/shaded region around 23 at.% Tb. This is a signature of the magnetic system approaching compensation composition (at room temperature) from both smaller and larger Tb content. At this composition the sub-lattices of Tb and Co compensate each other magnetically. Grey shaded areas show which compositions of samples with given thickness are onsets for in-plane magnetization.

The effect of film thickness on the sample magnetization state and the coercive field was investigated by fabricating samples of different thickness (5,
Figure 5.7. Coercive field dependence on Tb content in Tb$_x$Co$_{1-x}$ films prepared on double-side polished fused silica substrates and capped with a 3 nm thick, in-situ RF-sputtered AlO$_x$ layer. Grey regions indicate compositions of films exhibiting in-plane easy magnetization axis, while white area corresponds to compositions leading to an out-of-plane easy axis of magnetization. The shaded region at around 23 at.% Tb indicates the magnetization compensation point at room temperature.

7, 10, 20, 40, 73 nm). After PMOKE and LMOKE measurements it was determined that 10 nm thickness is the smallest thickness that gives a film an easy magnetization axis out-of-plane. At 7 nm thickness the out-of-plane axis becomes a hard magnetization axis and the magnetization of the sample lies in-plane. For the films with thickness larger than 20 nm the coercive field values are almost independent of film thickness which is due to limited penetration depth of light in MOKE measurements (See Fig. 5.7). The incident light can penetrate 10 - 20 nm of material before it gets scattered and absorbed, hence the signal coming from more than around 20 nm below the film surface is negligible.

$Tb_xCo_{1-x}$ with $Al_{80}Zr_{20}$ buffer and cap layers

The normalized hysteresis loops obtained in PMOKE measurements of Tb$_x$Co$_{1-x}$ films with varying Tb content ($x= 15, 18$ and 22 at.%) and prepared with $Al_{80}Zr_{20}$ buffer (and cap) layers are shown in Fig. 5.8. Measurements were carried out with the light of 530 nm wavelength. It can be noted that the sign of the hysteresis loops of the samples containing 15 and 18 at.% Tb is positive, that is, a positive external field results in a positive saturation magnetization. In contrast, the sample with 22 at. % of Tb shows a negative hysteresis loop, with saturation magnetization negative at a positive external magnetic field. This shows that the former two samples are of compositions above the com-
pensation point at room temperature, while the latter sample is below. Thus, they have different dominant species: Co-dominant when Tb content is 15 and 18 at. %, and Tb-dominant with 22 at. % Tb.

Figure 5.8. PMOKE measurements of Al$_{80}$Zr$_{20}$/Tb$_x$Co$_{1-x}$/Al$_{80}$Zr$_{20}$ films, where $x = 15$, 18 and 22 at.%. Loops were recorded using incident light with wavelength of 530 nm.

TbCo ferrimagnetic materials are magneto-optically (MO) active and therefore have a potential to be used for MO data storage [16, 20, 25]. Therefore, dispersion of Kerr rotation and ellipticity as measures of MO activity was investigated. Spectral Kerr effect measurements were carried out for samples from the AlZr series with AlZr seed and cap layers for 20 nm thick Tb$_x$Co$_{1-x}$ films with Tb content of 15, 18.6 and 22.4 at. % and results are shown in Fig. 5.9.

Figure 5.9. Kerr rotation and ellipticity dependence on the wavelength of incident light of 20 nm thick Tb$_x$Co$_{1-x}$ samples with $x = 15$, 18.6, 22.4 at.% Tb.
Monotonic dependence of Kerr rotation and ellipticity on incident light wavelength can be observed which is not surprising since the samples investigated here are continuous films. Features at the wavelengths larger than 750 nm are noise due to detector’s limits. Both Tb$_{15}$Co$_{85}$ and Tb$_{18}$Co$_{82}$ films show positive and increasing rotation and ellipticity with the wavelength of incident light while the Tb$_{22}$Co$_{78}$ sample shows the opposite behavior. The sign of rotation and ellipticity is an indication of the direction of the loop (See Fig. 5.8). Difference of sign of the rotation and ellipticity indicates that the films are on the opposite sides of the magnetization compensation point. The absolute values of Kerr rotation and ellipticity are less than 0.25 and 0.35$^\circ$, respectively, depending on the wavelength of incident light. The results obtained presented here are comparable to rotation and ellipticity values found in literature for other combinations of RE and TM. In the works by Hansen et al [9, 51], where the Kerr effect of RE-TM alloys, containing RE such as Gd, Tb and GdTb and TM Fe, Co and FeCo, was measured, similar values in the range from 0.1 to 0.6$^\circ$ of Kerr rotation were reported. However, MO activity reported in these alloys is still small and is even decreasing with decreasing wavelength which limits fabrication of magnetic elements with reduced dimensions [6, 11, 21].

5.5.2 MOKE microscopy

$Tb_xCo_{1-x}$ samples with $x > 22$ at. 

Kerr microscopy of TbCo samples was employed to investigate the domain size dependence on thickness and composition of the film. The magnetic domain size is important when considering nanostructuring of a continuous film: uniform magnetic domain size is essential for a magnetic nanoelement. Therefore, if the magnetic domains are large enough in a continuous film, after patterning the resulting nanomagnets should also exhibit a single domain state. Increasing thickness of TbCo film results into smaller magnetic domain structures at a remanent state. An example of domain structure at a remanent state of a 30 nm thick Tb$_{26}$Co$_{74}$ film capped with 3 nm AlO$_x$, after demagnetization, is shown in Figure 5.10(a). A random labyrinth-dendrite domain structure is revealed.

Dependence of average domain size on the Tb content above the compensation point at room temperature is shown in Figure 5.10. Kerr microscopy images were analysed employing a test line method and a pair correlation function as discussed in Chapter 4.5.

The higher the Tb content, the smaller is the magnetic domain. This trend appears to correlate with the one observed for the coercive field as was shown in Fig. 5.7. Hence, it can be concluded that the smaller domains are related to a lower coercive field of the films. These results show that one can control the size of a magnetic domain and coercive field by changing the composition of a film and that AOS can occur for a variety of films with magnetic domain
Figure 5.10. (a) Kerr microscopy image of magnetic domain state at remanence of a Tb$_{24}$Co$_{76}$ 20 nm thick film prepared on double-side polished fused silica substrate and capped with a 3 nm thick, in-situ RF-sputtered AlO$_x$ capping layer. The scale bar corresponds to 100 μm. (b) Summary of average magnetic domain sizes estimated using PCF and test line methods. Average domain width vs coercive field (that correspond to the different Tb:Co ratios) dependence as extracted from PCF graphs by approximation that an average domain width corresponds to the first minimum in PCF and using a test line method as described in the section 4.5.3.

sizes in a wide length range from less than 1 to 15 μm. Even though the domains appear to be random, the PCF shows that films exhibit a correlation length which corresponds to the average width of the magnetic domain as approximated by a first minimum in a PCF plot and hints about a certain range order of the magnetic domains.

5.6 Magnetization switching by light

The goal of this work was to determine which Tb:Co system parameters could lead to magnetization switching by light without the need for an external magnetic field. Therefore, series of all-optical magnetization switching experiments were performed in order to determine which range of compositions and thickness allows for the AOS of magnetization. The detailed description of AOS measurements is given in the Paper I.

The phase diagram given in Fig. 5.11(a) summarizes the results of all-optical magnetization switching processes observed in a range of TbCo films. It shows that all-optical helicity-dependent magnetization switching is achieved for the compositions above the compensation point when a high amount of pulses in a burst (minimum 50-100 shots) are used. The obtained diagram is in agreement with ones shown in the work by Mangin et al. [11]. AOS behavior of two different samples is compared in the Fig. 5.11(b). The sample on
the left is a 16 nm thick Tb$_{18}$Co$_{82}$ film while the sample on the right is 40 nm thick Tb$_{26}$Co$_{74}$ film. It can be observed that upon a circularly polarized laser light sweeping along the surface of the film in two opposite directions, only the higher content sample shows a helicity-dependent magnetization switching.

**Figure 5.11.** (a) Phase diagram summarizing which thickness and compositions of TbCo films allow the all-optical magnetization switching. Red area indicates the compositions for which pure thermal demagnetization occurs, while the green area indicates the compositions which exhibit all-optical magnetization switching, white area corresponds to a region where the magnetization of the sample is in-plane and hence showed no domain contrast. The minimum amount of laser pulses in a burst was 50-100 shots for each of the sample marked as switching. (b) Imaging of AOS experiments: (left) helicity independent thermal demagnetization of the 16 nm thick Tb$_{18}$Co$_{82}$ film and on the (right) all-optical helicity dependent switching for the 40 nm thick Tb$_{26}$Co$_{74}$ film, using a circularly polarized laser light of 800 nm wavelength and sweeping from right to left and then from left to right.

Effects of sweeping fluence and speed on the magnetization switching behavior of TbCo films with varying film thickness and Tb:Co ratio are presented. The threshold fluence required for observation of AO-HDS increases with increasing sample thickness. It was observed that for thicker samples a broad range of fluences and sweeping speeds enables homogeneous AO-HDS. For the samples with given thickness, no clear dependence on Tb:Co ratio was observed (See Fig. 5.12). Overall, the samples of 40 nm thickness require
higher fluence in order to achieve AO-HDS. These observations hint about accumulative magnetization switching.

Figure 5.12. Dependence on laser power (left) and sweeping speed (right) of AO-HDS switching in Tb$_x$Co$_{1-x}$ films of varying Tb content and thickness.

5.7 Optical characterization

Tb$_x$Co$_{1-x}$ films deposited directly on fused silica substrates without any capping layer were measured in order to obtain spectral dependence, or dispersion, of optical constants, a refractive index and extinction coefficient, $n$ and $k$, respectively. Since the project is aimed for the magnetization switching by light, the optical property dispersion is of interest. Thick samples (in the range of 30-50 nm) with varying Tb content, grown directly onto fused silica substrates without any capping layer (thus with the oxidized surface at the air interface) were measured and the computed $n$ and $k$ versus the incident light wavelength are shown in Fig. 5.13.

Insets show dependence of $n$ and $k$ on the Tb content in a film for 550 and 800 nm wavelengths of incident light. No clear dependence on the sample composition can be observed for the optical parameters, only a monotonic increase in both $n$ and $k$ with the increasing wavelength of light.

5.8 Hybrid Au/Tb$_x$Co$_{1-x}$ layers

Plasmonic materials are known to enhance magneto-optical activity in magnetic materials [22]. In this work, Au layers were used for plasmonic effect. However, it is important to check how the growth properties change upon changing the buffer layer. It was already shown in 5.5 that magnetic properties of TbCo films do not change drastically when comparing films prepared directly on a fused silica substrate and on a Au buffer layer (See Fig. 5.6(a)). The structure of films containing Au buffer layers were measured
using GIXRD and an example of a resulting diffractogram measured for a Tb$_{30}$Co$_{70}$ sample deposited onto a fused silica substrate with an electron-beam evaporated 30 nm thick Au film is shown in Fig. 5.8.

Three peaks, in contrast to a single peak for an identical sample but without a Au buffer layer, can be identified in the shown diffractogram: at around $2\theta = 22^\circ$ the peak originating from a fused silica amorphous substrate; at around $2\theta = 28^\circ$ - a (111) peak of the polycrystalline Au buffer layer and at around $2\theta = 44^\circ$ - broad low intensity peak corresponding to Tb$_{30}$Co$_{70}$. A peak at a similar position in $2\theta$ for a TbCo alloy film was observed in work by Frisk et al [52] for 9 at. % of Tb while initialization of crystallization of TbCo films was observed to occur for Tb content around 80 at. %.

Broad low intensity peaks indicate amorphous layers, whereas the sharp high intensity peaks indicates crystallinity. A sharp peak associated with the Au layer is a signature of the polycrystalline nature of this layer. A low intensity, relatively sharp peak associated with the Tb$_{30}$Co$_{70}$ layer indicates some degree of crystallinity of this layer. The crystallite size, $D$, in the film can be calculated using Scherrer’s equation:

$$D = \frac{K \lambda}{B \cos \theta}$$

where $K$ is a constant (usually taken as 0.94), $\lambda$ is the wavelength of the X-rays, $B$ is the full width at half maximum of the diffraction peak, and $\theta$ is the Bragg angle.
where \( K \) is the form factor depending on the crystallite shape and typically is around 0.9, \( \lambda \) is the wavelength of x-rays, \( w \) is the full-width-at-half-maximum (FWHM) of the peak (in rad) and \( \theta \) is the Bragg angle \((0.5 \times 2\theta)\).

Using the Scherrer equation and FWHM values given in Fig. 5.8, the following values were obtained for Au buffer and Tb\(_{30}\)Co\(_{70}\): 97.9 and 58.7 Å, respectively. This indicates that at the Au/Tb\(_{30}\)Co\(_{70}\) interface Tb\(_{30}\)Co\(_{70}\) alloy could have formed nanocrystallites similarly as has been reported in the work by Liebig et al [53].

\[
D = \frac{K\lambda}{w\cos\theta},
\]

(5.1)

Figure 5.14. GIXRD measurement of Tb\(_{30}\)Co\(_{70}\) and Au/Tb\(_{30}\)Co\(_{70}\) samples. The incident angle \( \omega \) was 1.5° while detector was scanning at the range \( 2\theta = 10-60^\circ \). Diffractograms were deconvoluted to Lorentzians and peaks associated with fused silica substrate, Au buffer layer and Tb\(_{30}\)Co\(_{70}\) film are identified. The intensity was normalized to the fused silica peak.
The effect of increasing grazing angle can be observed by plotting the integrated area of each of the peaks versus the grazing angle as shown in Fig. 5.8. The peak area is increasing with the increasing incident angle of x-rays since thicker and thicker layer of the material is probed.

The area of the peak associated with the Au buffer layer appears to be approaching a constant value with increasing angle. Similar observations are valid for the area of a peak corresponding to the Tb$_{30}$Co$_{70}$ layer. Meanwhile, the area of the peak corresponding to the fused silica substrate is still monotonously increasing. This indicates that signals from the Au buffer and Tb$_{30}$Co$_{70}$ layers are maximized and the whole thickness of these layer are probed whereas higher grazing angles are required to measure the full thickness of the fused silica substrate.
6. Summary and Conclusions

Results of this study reveal that Tb:Co is a flexible material system that has potential for all-optical-switching of magnetization. It was demonstrated that the coercive field is dependent on the Tb:Co ratio in a film as well as on what seed layer the film is deposited onto. Coercive field and easy magnetization axis can also be modified by changing the Tb:Co thickness: reducing thickness results in decreasing $\mu_0H_c$ and change in easy magnetization axis from out-of-plane to in-plane. A critical thickness (7 nm) exists where both in- and out-of-plane magnetization components can be measured using MOKE. Changing Tb:Co ratio to both directions (increasing and decreasing) away from the magnetization compensation composition at room temperature results in decreasing coercive field. At the same time, out-of-plane magnetic anisotropy is decreasing until easy axis of magnetization becomes in-plane for Tb content smaller than 15 at. % and larger than 37 at. %. The magnetization compensation point is also dependent on the buffer layer onto which the Tb:Co film is sputtered. Having an AlZr seed reduces the magnetization compensation point to a region around 20 at.% Tb as compared to a region around 23 at.% Tb for films deposited onto other amorphous buffer layers such as AlO$_x$, or fused silica substrates. Domain sizes of the Tb:Co films at a remanence state are in the range of 1-13 μm. This makes the films suitable for patterning structures of nanoscale since uniform magnetization throughout the magnetic nano-element is guaranteed.

Optical constants, refractive index $n$ and extinction $k$ coefficient are wavelength dependent and show a monotonic increase with increasing wavelength of incident light. No monotonic dependence on the Tb:Co ratio in a film was observed. The magneto-optical parameters, Kerr rotation and ellipticity are wavelength dependent and increase with increasing wavelength of the incident light. Absolute values smaller than 0.4 degrees were measured for a stack with AlZr seed and cap layers. Single-shot helicity-independent toggle switching was not observed for any of the TbCo samples (both with and without buffer layer). AO-HDS is observed for samples grown directly on fused silica substrates (without the AlZr seed layer), having Tb composition higher than 22 at.%. The fluence and speed dependence of switching points towards an accumulative switching mechanism. Evolution from helicity-independent demagnetization to helicity dependent switching is observed when the minimal number of incident laser pulses is 50-100. Increasing thickness of the samples seems to make AO-HDS feasible for a larger range of fluences and switching speeds. However, the effect of composition within the samples that do show AO-HDS is unclear.
7. Outlook

Results of this research provide a comprehensive summary about Tb:Co amorphous alloy growth processes and conditions and a pathway for controlling structural and magnetic properties of this system. Knowledge about the structural arrangement and magnetic and magneto-optical behaviour of this system allows for planning further patterning of nanostructures from such films. This in turn allows for the next step in preparations and investigation of novel fundamental building blocks of memory elements where magnetization switching is facilitated by polarized light.

Initial efforts were already spent on fabrication of nanostructures using Tb$_{18}$Co$_{82}$ layers. First of the kinds of the fabricated arrays was magneto-optically active nanocones, presented in the work by R. M. R. Robinson et al. [54]. Truncated nanocones were prepared from a Au(80 nm)/Tb$_{18}$Co$_{82}$(15 nm)/Al$_2$O$_3$(2 nm) film via electron beam lithography (EBL). In Figure 7.1 dependence of Faraday rotation and ellipticity for the arrays with increasing base diameter can be seen. It can be observed that the resonant feature shifts towards longer wavelengths when the base diameter increases in the rectangular lattice with 340 and 425 nm lattice parameter along the short and long axis, respectively. This shows that even though the amount of the ferrimagnetic Tb$_{18}$Co$_{82}$ is significantly reduced (the diameter of a truncated Tb$_{18}$Co$_{82}$ nanocone on top of the truncated Au cone is around 80 nm after the patterning), the magnetization and out-of-plane magnetic anisotropy are preserved.

A second kind of structures patterned from the Tb$_{18}$Co$_{82}$ layers was Au(20 nm)/Tb$_{18}$Co$_{82}$(20 nm)/Al$_2$O$_3$(2 nm) 250 nm size in diameter nanodiscs and nanorings with 250 nm outer radius and the inner diameter of 30 and 60 nm as shown in Fig. 7.2I. Samples were measured in a Faraday geometry using p-polarized light of 600 nm wavelength. The resulting magnetization loops of each of the structures are shown in 7.2 II. It can be seen that out-of-plane magnetization is retained for discs and thick rings whereas it becomes weaker for the thin rings, which appear to be at the limit of becoming paramagnetic. Furthermore, such a magnetization loop for the thin ring array was observed only at wavelengths around 600 nm, whereas for other wavelengths a paramagnetic curve was observed. This hints about a plasmonic enhancement of the magneto-optical activity in TbCo due to the underlying Au layer.

Results of this work show potential of the Tb:Co system for all-optical switching of magnetization, where ultrafast, femtosecond duration, laser pulses are required. Furthermore, owing to its ferrimagnetic nature, terahertz, or picosecond duration, magnetization dynamics could be investigated in Tb:Co alloys.
Figure 7.1. Faraday rotation and ellipticity for the truncated nanocones arranged into an identical rectangular lattices but with varying nanocone base diameter.

Figure 7.2. Panel I: SEM micrographs of (a) nanodiscs and (b-c) nanorings EBL patterned from Au(20 nm)/Tb$_{18}$Co$_{82}$(20 nm)/Al$_2$O$_3$(2 nm) continuous films. Panel II: Magnetization loops measured at 600 nm wavelength of incident p-polarized light.
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References


