(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 August 2004 (19.08.2004)

PCT

(10) International Publication Number
WO 2004/069767 A1

(51) International Patent Classification[7]: C04B 35/453, H01F 10/10

(21) International Application Number: PCT/SE2004/000150

(22) International Filing Date: 6 February 2004 (06.02.2004)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0300352-2 6 February 2003 (06.02.2003) SE

(71) Applicant *(for all designated States except US)*: **NILSSON MATERIALS AB** [SE/SE]; Emdalavägen 16, S-223 69 Lund (SE).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **SHARMA, Parmanand** [IN/IN]; Q. No. I-6, Type-II, Kiningsway Camp New Police Lines, Delhi 110 009 (IN). **RAO, Kudumboor Venkat** [SE/SE]; Roslagsgatan 58, 2 tr, S-113 54 Stockholm (SE). **JOHANSSON, Börje** [SE/SE]; Tomatgatan 17, S-754 49 Uppsala (SE). **AHUJA, Rajeev** [IN/SE]; Rackarbergsgatan 94 330, S-752 32 Uppsala (SE).

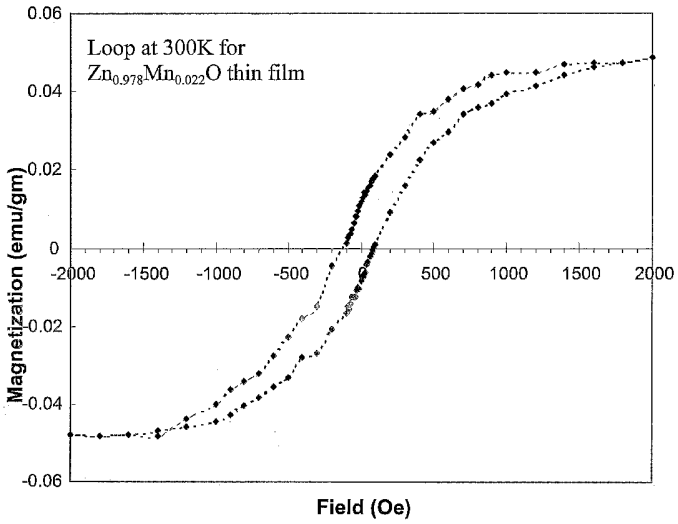
(74) Agents: **LINDBERG, Olle** et al.; Albihns Malmö AB, P.O. Box 4289, S-203 14 Malmö (SE).

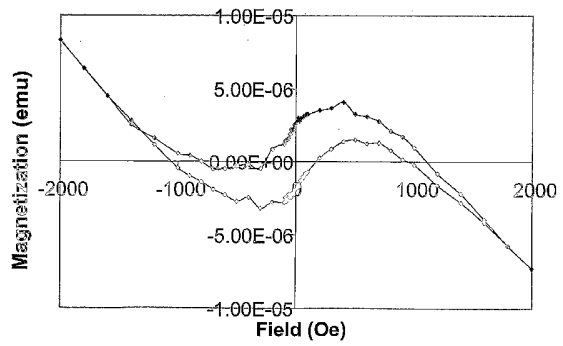
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH,

[Continued on next page]

(54) Title: FERROMAGNETIC MATERIAL





(57) Abstract: Method for producing a doped dilute ferromagnetic semiconductor material, by doping Zinc Oxide in bulk form with Manganese to a maximum level of 5 atomic percent concentration. The material is preferably sintered at a maximum temperature of 650 °C. The result of this process is a semiconductor material comprising Mn-doped ZnO with a Mn concentration not exceeding 5 at%, wherein said Mn-doped ZnO is ferromagnetic within at least a part of the temperature range from about 218 Kelvin to about 425 Kelvin.

WO 2004/069767 A1

GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(ii)) for all designations*

— *as to the applicant's entitlement to claim the priority of the earlier application (Rule 4.17(iii)) for all designations*

— *of inventorship (Rule 4.17(iv)) for US only*

Published:

— *with international search report*

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

The Swedish Patent Office
PCT International Application

PCT / SE 2004 / 0 0 0 1 5 0
29 -03- 2004

Continuation of Box No. VIII (iv)

REC'D 14 APR 2004
WIPO PCT

Name JOHANSSON Börje

Residence Sweden

Mailing Address Tomatgatan 17
SE-754 49 Uppsala, Sweden

Citizenship Swedish

Inventor's signature ..... Date 04-03-22

Name AHUJA Rajeev

Residence Sweden

Mailing Address Rackarbergsgatan 94 330
SE-752 32 Uppsala, Sweden

Citizenship ~~Swedish~~ (Indian)

Inventor's signature ..... Date 04-03-22

FERROMAGNETIC MATERIAL

Field of invention

The present invention relates to materials used for electronic components which use ferromagnetism in its function.

Background

Components based on materials with ferromagnetic properties are devised to affect or rectify the spin orientation of bosons and fermions, e.g. electrons. The search for materials with ferromagnetism above room temperatures in dilute magnetic semiconductors has been a quest in recent years, especially to develop a potentially rich new class of future devices which exploit the electron spin state i.e. spintronics. The types of components for these devices include magnetic memories, e.g. hard discs, semiconductor magnetic memories, e.g. MRAM, spin valve transistors, spin light emitting diodes, non-volatile memory, logic devices, quantum computers, optical isolators, sensors, ultra-fast optical switches etc. Dilute magnetic semiconductors can also be used in electronic-, and magnetic -based products.

Description of related art

Electronic component technologies are increasingly interested in using ferromagnetic materials for new component designs and functions. Traditional ferromagnetic materials are e.g. iron, nickel, cobalt and their alloys. Novel scientific activities and new suggestions for implementing them, are frequently being reported in technical and scientific journals. Some examples of materials expectations with basic component designs can be found in recent review articles in Physics World, (April 1999) and IEEE Spectrum, (December 2001). All these documentations describe the problem and needs in designing ferromagnetic materials that can operate at the industrial, automotive and military temperature range, normally -55 °C to 125 °C. Other pieces of prior art within this technical field are listed in a list of references below.

Most of the materials of interest known today require cryogenic temperatures. However Klaus H. Ploog described in Physical Review Letters, July 2001, the use of a film of iron grown on Gallium Arsenide (GaAs) to polarize the spin of electrons injected into semiconducting GaAs. This experiment was carried out at room temperature.

Spintronic devices such as spin valve transistors, spin light emitting diodes, non-volatile memory, logic devices, optical isolators and ultra-fast optical switches are some of the areas of high interest for introducing the ferromagnetic properties at room temperature in a semiconductor described in the two documents of reference 6 and 7.

In recent years there have been intense search for materials exhibiting ferromagnetic ordering in doped dilute magnetic semiconductors (DMS), described in the five documents of reference 1-5, focusing on possible spin transport properties which has many potentially interesting device applications. Among the materials reported so far, Mn-doped GaAs has been found to be ferromagnetic with the highest reported Curie temperature, Tc ~ 110 K, see reference 1. Following this, Dietl et al. predicted on a theoretical basis that ZnO and GaN would exhibit ferromagnetism above room temperature on doping with Mn, see reference 2. This prediction initiated intensive experimental work on a variety of doped dilute magnetic semiconductors. Recently, Tc above room temperature has been reported in Co-doped TiO_2 , ZnO, and GaN respectively, see references 3,8,9. However, in the $Ti_{1-x}Co_xO$ sample inhomogeneous clustering of Co was found, see reference 10. Kim et al, see reference 11, showed that while homogeneous films of $Zn_{1-x}Co_xO$ exhibited a spin-glass behaviour, room temperature ferromagnetism was found in inhomogeneous films attributing the observation to the presence of Co clusters.

References

1. Ohno, H. Making Nonmagnetic semiconductors ferromagnetic.
Science 281, 951-956 (1998); see also a recent review:
S.J. Pearton et al JAP 93, 1 (2003).

2. Dietl, T. et al. Zener model description of ferromagnetism in zinc-blende magnetic semiconductors. Science 287, 1019-1022 (2000)

3. Matsumoto, Y. et al. Room-temperature ferromagnetism in transparent transition metal-doped titanium dioxide. Science 291, 854-856 (2001)

4. Ando, K. et al. Magneto-optical properties of ZnO-based dilute magnetic semiconductors. J. Appl. Phys. 89(11), 7284-7286 (2001)

5. Takamura, K. et al. Magnetic properties of (Al,Ga,Mn)As. Appl. Phys. Letts 81(14), 2590-2592 (2002)

6. Chambers, S. A. A potential role in spintronics. Materials Today, 34-39 (april 2002)

7. Ohno, H. Matsukura, F. & Ohno, Y. Semiconductor spin electronics. JSAP international 5, 4-13 (2002)

8. Ueda, K. Tabata, H. & Kawai, T. Magnetic and electric properties of transition-metal-doped ZnO films. Appl. Phys. Letts 79(7), 988-990 (2001)

9. Thaler, G. T. et al. Magnetic properties of n-GaMnN thin films. Appl. Phys. Letts. 80(21), 3964-3966 (2002)

10. Stampe, P. A. et al. Investigation of the cobalt distri bution in TiO2:Co thin films. J. Appl. Phys. 92(12), 7114-7121 (2002)

11. Kim, J. H. et al. Magnetic properties of epitaxially grown semiconducting Zn1-xCoxO thin film by pulsed laser deposition. J. Appl. Phys. 92(10), 6066-6071 (2002)

12. Fukumura, T. et al. An oxide-diluted magnetic semiconductor: Mn-doped ZnO. Appl. Phys. Letts. 75(21), 3366-3368 (1999)

13. Fukumura, T. et al. Magnetic properties of Mn doped ZnO. Appl. Phys. Letts. 78(7), 958-960 (2001)

14. Jung, S.W. et al. Ferromagnetic properties of Zn1-xMnxO epitaxial thin films. Appl. Phys. Letts. 80(24), 4561-4563(2002)

15. Tiwari, A. et al. Structural, optical and magnetic properties of diluted magnetic semiconducting Zn1-xMnxO films. Solid State Commun. 121, 371-374 (2002)

Summary of invention

Accordingly, there are still advances to be made within the field of ferromagnetic materials. It is therefore a general object of the present invention to provide a material with ferromagnetic properties, and means for producing such a material, which overcomes certain disadvantages related to the prior art. In particular, it is clear that for many device applications homogeneous material films are needed, and an aspect of the general object is therefore to provide means for producing such homogeneous material films.

The present invention is based on the concept to create ferromagnetism into doped dilute magnetic semiconductors by doping Zinc Oxide (ZnO) with Manganese (Mn). Tailoring of ferromagnetism above room temperature in bulk Mn (<4 atomic %) doped ZnO has been achieved. In this state Mn is found to carry a moment $0.16\mu_B$. Ferromagnetic Resonance (FMR) data on these samples have confirmed the surprising results of the existence of ferromagnetic order at temperatures even as high as 425K. In the paramagnetic state the Paramagnetic Resonance data show that Mn is in the 2+ state (Mn^{2+}) with a g value 2.0029. Ab initio calculations confirm the above findings. On sintering the bulk at temperatures above 700°C, the ferromagnetism around room temperatures is completely suppressed giving rise to the often reported pronounced 'ferromagnetic-like' ordered state below 40K. The material also shows room temperature ferromagnetic ordering in 2-3 μm thick transparent films deposited on fused quartz substrates at temperatures below 600 °C by Pulsed Laser deposition using the same bulk materials as targets. The ferromagnetic dilute Mn doped ZnO can also be obtained as transparent nanoparticles.

The demonstrated new capability renders possible the realization of complex elements for spintronic devices and other components. Manganese doped Zinc oxide, with ferromagnetic properties in the specified temperature range can also be manufactured with a sputtering system where either two metallic (Zinc and Manganese) targets are used simultaneously or one sintered ZnO:Mn ceramic target.

The present invention is defined by the appended claims.

Brief description of drawings

Preferred embodiments of the present invention will be described below with reference to the accompanying drawings, on which:

Fig. 1 shows a room temperature hysteresis loops showing ferromagnetic ordering in nominal 2% Mn doped ZnO pellets sintered at various temperatures according to an embodiment of the invention;

Fig. 2 shows a M(H) hysteretic loop data at 300K for Zn0.978Mn0.022O PLD deposited thin film on fused quartz, after subtracting the diamagnetic contribution (shown as an insert) arising from the fused quartz substrate in the 'as obtained' data from SQUID measurements;

Fig. 3 shows a) the Ferromagnetic resonance spectra for nominal 2 at% Mn doped ZnO pellet sintered at 500°C, and (b) the paramagnetic resonance spectra for the same sample sintered at 900 °C; and

Fig. 4 shows the calculated density of states (DOS) for Zn0.958Mn0.042O, Fermi level is set at zero, where inset shows the DOS near to the Fermi level, and the states just below the Fermi level arising from the Mn 3d states. Below to Mn-3d states, the states between 4 to 6 eV are from O-2p states and states between 6 to 8 eV are arising from Zn-3d states.

Detailed description of preferred embodiments

The present invention is based on the concept to create ferromagnetism in doped dilute magnetic semiconductors by doping Zinc Oxide (ZnO) with Manganese (Mn) in bulk or film materials. Our experiments shows successful tailoring of ferromagnetism above room temperature in bulk Mn doped ZnO. The

Mn doping level should then be less than 4-5 at% (atomic percent) for bulk materials. Theoretically we find that the upper limit for ferromagnetism is about 5 at% Mn. Experimentally we have found that due to materials problems, above 4 at% Mn there is a clear tendency for the Mn atoms to form clusters which are then antiferromagnetic and that suppresses the ferromagnetic order. SEM observations show, on samples above 2 at%, local clustering and the samples becomes inhomogeneous, which affects the material so that the around room temperatures ferromagnetic effect disappears at 4-5at%. In ZnO, the thermal solubility of 3d-transition metals such as Mn is larger than 10 mol% and the electron 'effective mass' is as large as ~$0.3m_e$, where m_e is free electron mass, see reference 12. Therefore the amount of injected spins and carriers in the film can be large, thus making Mn doped ZnO ideal for the fabrication of spintronic devices. Moreover ZnO is a well-known piezoelectric and electro-optic material, and therefore incorporation of magnetic property in ZnO can lead to variety of new multifunctional phenomena.

Theoretical predictions claim that only p-type Mn doped ZnO will be ferromagnetic above room temperature. However, our experiments show that n-type ZnO can also be ferromagnetic above room temperature, but the ferromagnetism tends to decrease as the n-type carrier in the material increases. In the room temperature ferromagnetic state of our samples Mn is found to carry a moment 0.16μB. Ferromagnetic Resonance (FMR) data confirm the existence of ferromagnetic order at temperatures as high as 425K in both pellets and thin films. In the paramagnetic state the EPR spectra show that Mn is in the 2^+ state ($Mn2^+$). Furthermore, ferromagnetism above room temperature is also observed in the calcined (below 500°C) powder. Our ab initio calculations confirm the above findings. If sintering of the Mn doped ZnO material is carried out at higher temperatures the doped material shows an additional large paramagnetic contribution at room temperatures and the ferromagnetic component becomes negligible. On sintering the bulk at temperatures above 700°C, ferromagnetism around room temperatures is completely suppressed giving rise to the often reported

pronounced 'ferromagnetic-like' ordered state below 40K. Experiments with sintering temperatures of 700 °C, 800 °C and 900 °C have confirmed this fact.

Room temperature ferromagnetic ordering has also been obtained in 2-3 μm thick films deposited on fused quartz substrates at temperatures below 600 °C, by Pulsed Laser deposition using the same bulk materials as targets. The doping concentration in these film materials should be less than 3-4at% in order to obtain controlled homogeneity. Experiments have shown that samples below 2 at% can be tailored to be homogeneous in composition with slight variations but containing no clusters. In laser ablation the substrate temperature effects the Mn concentration in the film. Films deposited at higher temperatures are found to have a high concentration of Mn in comparison to films deposited at low temperatures. This means that the temperature could be used to control the Mn concentration.

The precursor ZnO and MnO_2 powders (purity 99.99%) used in the present study to make Mn doped ZnO were characterized initially for their magnetic properties using quantum design, MPMS2-SQUID magnetometer. SQUID measurements showed diamagnetic behavior for the ZnO powder, while MnO_2 was found to be anti-ferromagnetic below 100K as expected. Appropriate amounts of ZnO and MnO2 powders were mixed, calcined at 400 °C for 8 hours, and sintered in air at different temperatures ranging from 500 to 900 °C for 12 hours to obtain $Zn_{1-x}Mn_xO$ (nominal x = 0.01, 0.02, and 0.1 at% respectively) ceramic pellets.

The effect of sintering temperature on the magnetic properties of nominal 2% Mn doped ZnO has been specifically studied, and ferromagnetic ordering above room temperature (Tc > 420K) has been found. The room temperature ferromagnetic phase as a function of sintering temperatures, as indicated by M(H) measurements, are shown in fig.1. Elemental mapping for the pellet sintered at 500 °C showed a uniform distribution of Mn in the sample. However local Mn concentration was found to be much lower (~ 0.3 at%) than the nominal composition. Taking this fact into consideration, we evaluate the saturation magnetization of the ferromagnetic phase and determine the moment per Mn atom to be 0.16 μB. Sometimes on sintering the pellets in the temperature range 600 °C - 700 °C in addition to the ferromagnetic component we observe a linear

paramagnetic contribution in the magnetic hysteretic loops at high fields. However, sintering the pellets above 700 °C completely suppresses ferromagnetism around room temperature. The doped dilute semiconductor can also be processed, by particle size selection, into transparent and ferromagnetic nanoparticles.

Manganese doped Zincoxide can be manufactured with a sputtering system where either two metallic (Zinc and Manganese) targets are used simultaneously or one sintered ZnO:Mn ceramic target as described previously. When using two metallic targets the sputtering energy on the Zn and Manganese targets are adjusted in such a way that the resulting Manganese content is in the 1-5% range. An exact recipe has to be adjusted to the sputtering equipment that is used and depends on energy, geometry and gases. This technique is, however, well known to the skilled person. The substrate temperature on the deposition substrate is in the same range as when using laser deposition.

X-ray Diffraction as well as SEM high resolution elemental mapping analyses on both the bulk as well as thin film Mn doped ZnO materials obtained by us are found to be homogeneous with no sign of cluster formation or distribution in them.

Incidentally, in both the bulk and the transparent films we obtained their ferromagnetic resonance spectra which provide convincing evidence for the existence of ferromagnetism. The demonstrated new capability renders possible the realization of complex elements for spintronic devices. These type of films materials are transparent and could be used for magneto-optical components. ZnO has a large electromechanical coupling coefficient and is therefore also good for piezoelectric applications and combinations for optical, magneto and mechanical sensor or component solutions.

Total energy calculations were performed using the projector augmented-wave (PAW) method as invoked by the VASP program package based on the generalized-gradient approximation (GGA). The parameterization for the exchange and correlation potential proposed by Perdew et al was employed. In the present calculations we made use of PAW potentials which valence states 3p, 3d and 4s for Mn, 3d and 4s for Zn and 2s and 2p for O. The periodic supercell approach is employed and the energy cutoff was 600 eV. The optimization of the geometry has

been done (ionic coordinates and c/a ratio), using the Hellmann-Feynman forces on the atoms and stresses on the supercell for each volume. For sampling the irreducible wedge of the Brillouin zone we used k-point grids of 4x4x2 for the geometry optimization and 8x8x4 for the final calculation at the equilibrium volume.

Various embodiments of the present invention, both regarding the inventive material as such and means for producing it in various forms, have been discussed above. However, these should merely be regarded as examples and not as limitations. The scope of the invention is defined by the appended claims.

CLAIMS

1. Method for producing a doped dilute ferromagnetic semiconductor material, comprising the step of:
- doping Zinc Oxide in bulk form with Manganese to a maximum level of 5 atomic percent concentration.

2. The method as recited in claim 1, comprising the step of:
- sintering the material at a maximum temperature of 650°C.

3. The method as recited in claim 1, comprising the step of:
- producing said material by laser deposition on a substrate.

4. The method as recited in claim 1, comprising the step of:
- producing said material by sputtering to a deposition substrate, simultaneously using two metallic targets of Zinc and Manganese, respectively;
- controlling the temperature on the deposition substrate to a maximum of 650°C; and
- adjusting a sputtering energy on the Zinc and Manganese targets such that a resulting Manganese content in the 1-5 atomic% range is achieved.

5. The method as recited in claim 1, comprising the step of:
- producing said material by sputtering to a deposition substrate, using a sintered ZnO:Mn ceramic target;
- controlling the temperature on the deposition substrate to a maximum of 650°C; and
- adjusting a sputtering energy on the target such that a resulting Manganese content in the 1-5 atomic% range is achieved.

6. The method as recited in claim , comprising the step of:
- producing said material in powder form by means of a calcining process, prior

to sintering the material.

7. The method as recited in claim 6, comprising the step of:
- performing said calcining process at a temperature below 500°C.

8. The method as recited in any of claims 1-7, comprising the step of:
- processing said material further to form transparent and ferromagnetic *nanoparticles by means of particle size selection.*

9. A semiconductor material comprising Mn-doped ZnO with a Mn concentration not exceeding 5 at%, **characterised in** that said Mn-doped ZnO is ferromagnetic within at least a part of the temperature range from about 218 Kelvin to about 425 Kelvin.

10. The material as recited in claim 9, further **characterised in** that it is transparent.

11. The material as recited in claim 9 or 10, further **characterised in** that it is piezoelectric.

12. The material as recited in any of claims 9-11, **characterised in** that said material is produced using the method as recited in any of the claims 1-8.

13. A substrate having at least one thin layer deposited on at least one part of its surface, **characterised in** that said layer comprises a material according to any of claims 9-12.

14. A component to be used for electronic applications, **characterised in** that said component comprises a material according to any of claims 9-12.

15. A component to be used for spintronic applications, **characterised in** that said component comprises a material according to any of claims 9-12.

16. A component to be used for optical applications, **characterised in** that said component comprises a material according to any of claims 9-12.

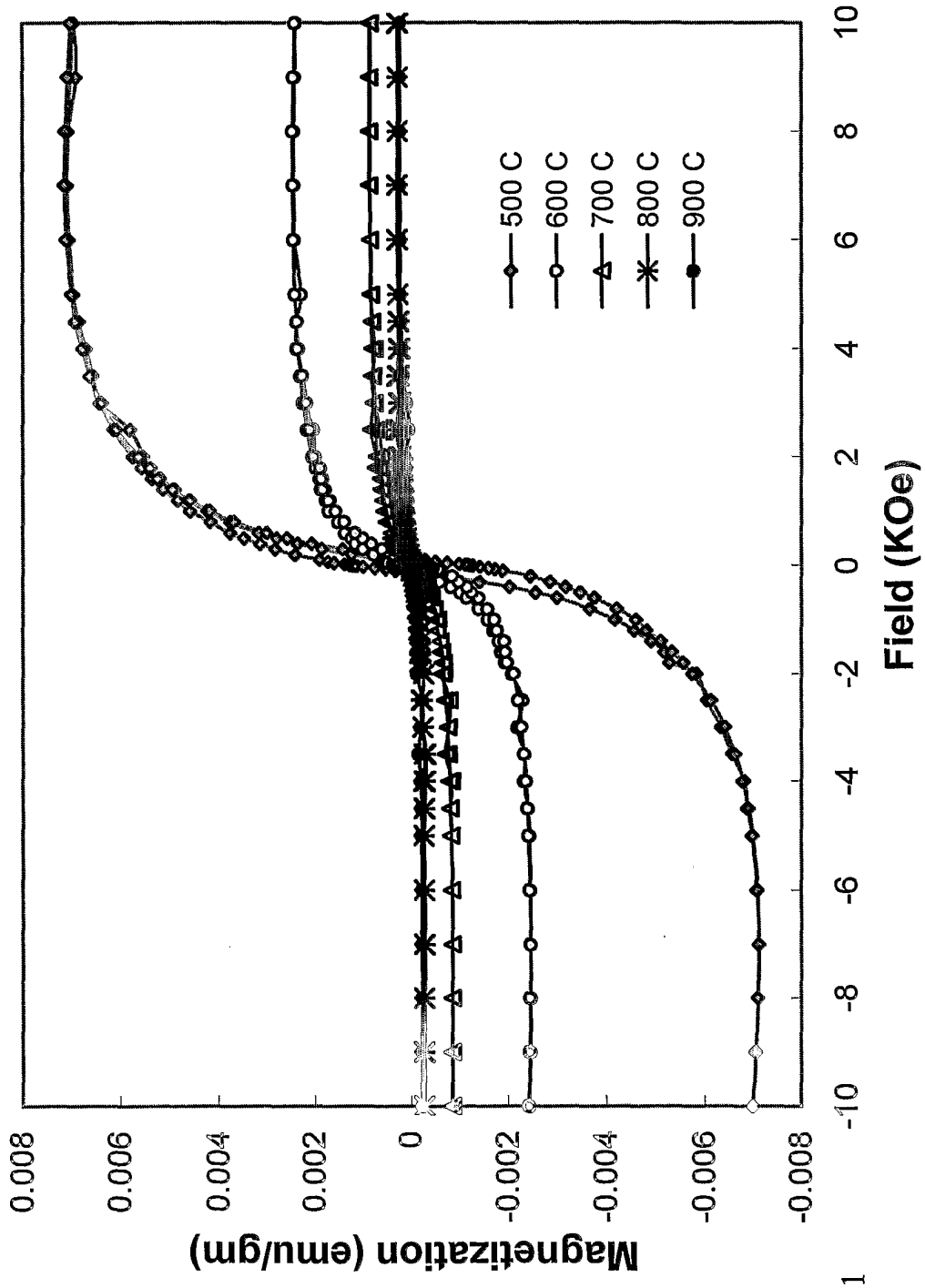
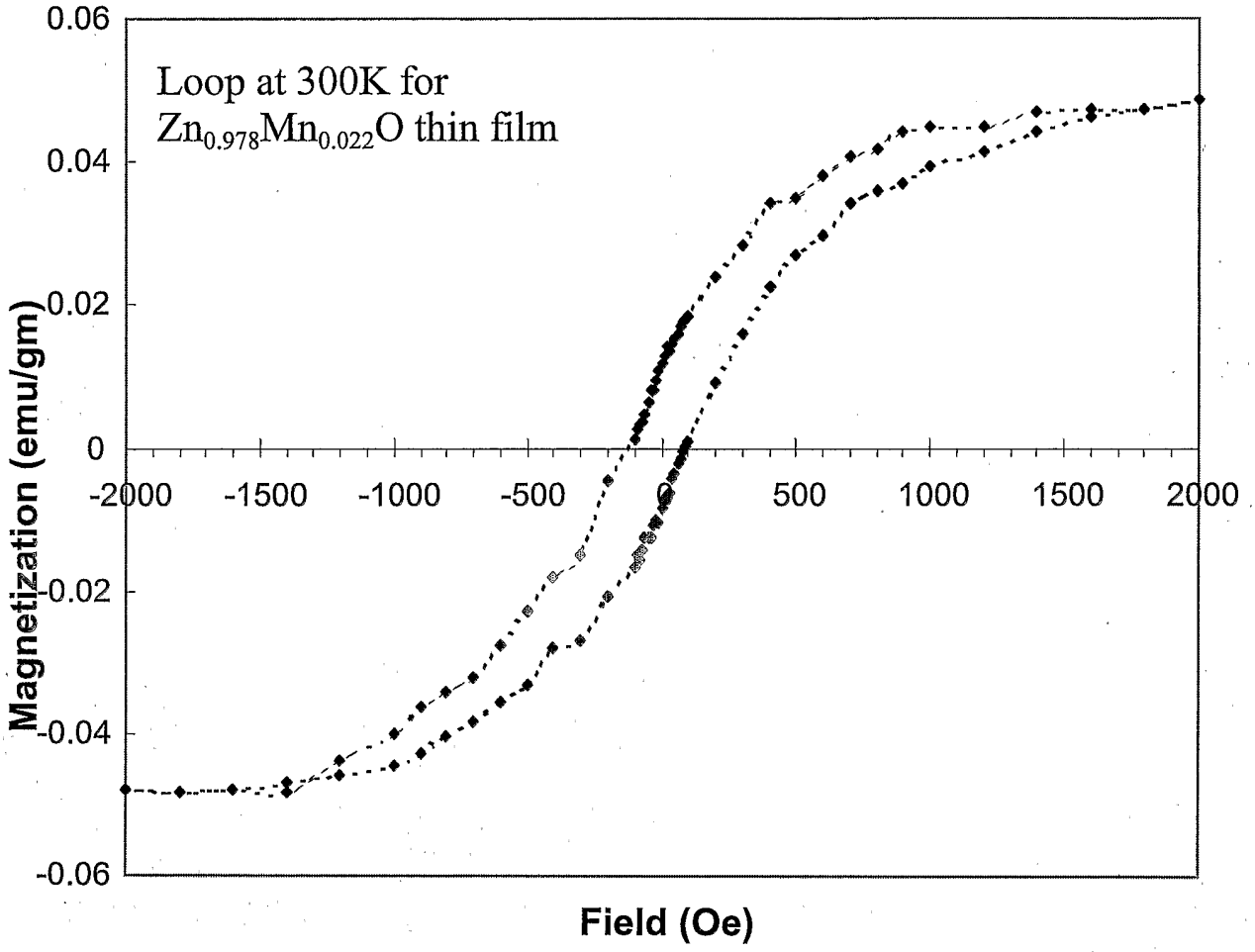

Magnetization (emu/gm)
0.008
0.006
0.004
0.002
0
-0.002
-0.004
-0.006
-0.008
Field (KOe)
10
8
6
4
2
0
-2
-4
-6
-8
-10
500 C
600 C
700 C
800 C
900 C

Fig. 1


Loop at 300K for
$Zn_{0.978}Mn_{0.022}O$ thin film
0.06
0.04
0.02
0
-0.02
-0.04
-0.06
-2000
-1500
-1000
-500
0
500
1000
1500
2000
Magnetization (emu/gm)
Field (Oe)

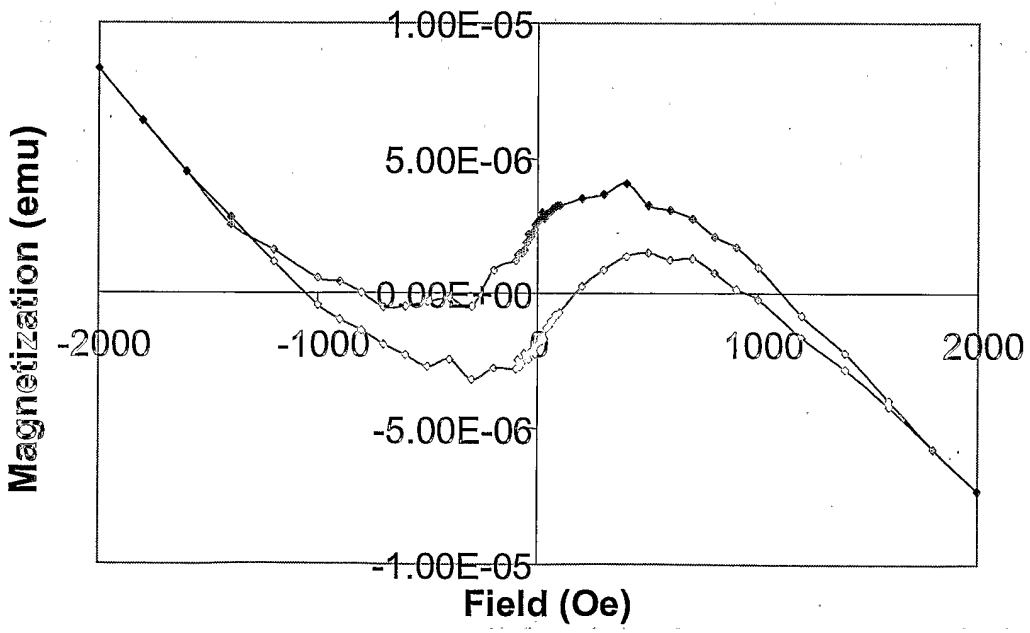

1.00E-05
5.00E-06
0.00E+00
-5.00E-06
-1.00E-05
-2000
-1000
1000
2000
Magnetization (emu)
Field (Oe)

Fig. 2

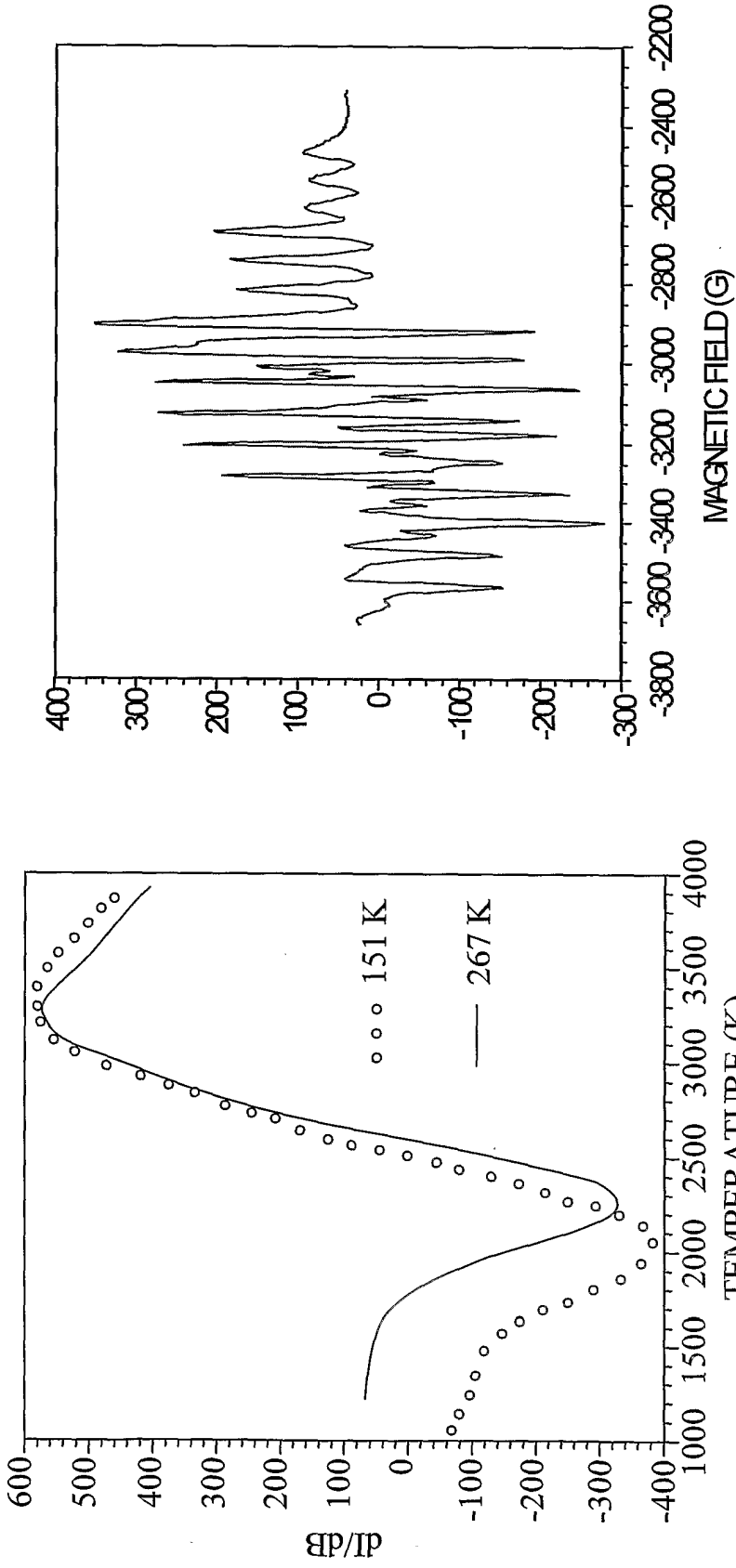

MAGNETIC FIELD (G)
-2200
-2400
-2600
-2800
-3000
-3200
-3400
-3600
-3800
400
300
200
100
0
-100
-200
-300
dI/dB
600
500
400
300
200
100
0
-100
-200
-300
-400
1000 1500 2000 2500 3000 3500 4000
TEMPERATURE (K)
151 K
267 K

Fig. 3

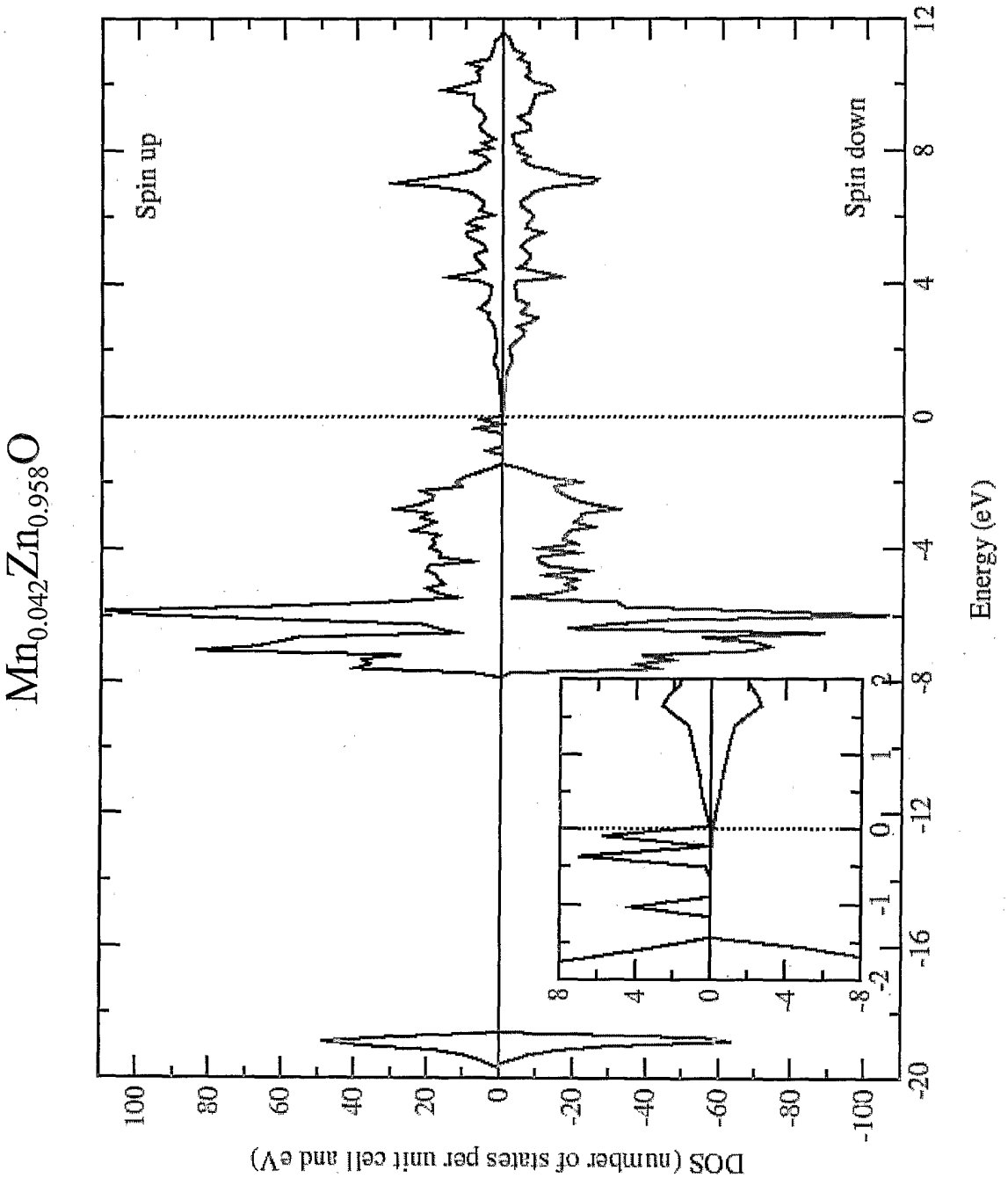

$Mn_{0.042}Zn_{0.958}O$
Spin up
Spin down
DOS (number of states per unit cell and eV)
Energy (eV)
100
80
60
40
20
0
-20
-40
-60
-80
-100
12
8
4
0
-4
-8
-12
-16
-20
8
4
0
-4
-8
2
1
0
-1
-2

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SE 2004/000150

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C04B 35/453, H01F 10/10
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC7: C04B, H01F, H01L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

SE,DK,FI,NO classes as above

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-INTERNAL, WPI DATA, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 1219731 A1 (JAPAN SCIENCE AND TECHNOLOGY CORPORATION), 3 July 2000 (03.07.2000), see section [0005-022] ---	1,3,8-16
A	Katsuyasu Kawano et al, "Electron spin resonance study of laser-annealed (Zn,Mn)O ceramics", 1991, Appl.Phys.Lett 58, (Tokyo), page 1742 - page 1744 --- --------	1-16

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance: the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance: the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
31 March 2004	04 -05- 2004
Name and mailing address of the ISA/ Swedish Patent Office Box 5055, S-102 42 STOCKHOLM Facsimile No. +46 8 666 02 86	Authorized officer Fredrik Wahlin/MN Telephone No. +46 8 782 25 00

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT
Information on patent family members

27/02/2004

International application No.
PCT/SE 2004/000150

EP	1219731	A1	03/07/2000	JP	2001072496	A	21/03/2001
				WO	0116411	A	08/03/2001