Increased static dielectric constant in ZnMnO and ZnCoO thin films with bound magnetic polarons

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A novel small signal equivalent circuit model is proposed in the inversion regime of metal/(ZnO, ZnMnO, and ZnCoO) semiconductor/SiN, insulator/p-Si semiconductor (MSIS) structures to describe the distinctive nonlinear frequency dependent capacitance (C-F) and conductance (G-F) behaviour in the frequency range from 50 Hz to 1 MHz. We modelled the fully depleted ZnO thin films to extract the static dielectric constant ($\varepsilon_r$) of ZnO, ZnMnO, and ZnCoO. The extracted enhancement of static dielectric constant in magnetic n-type conducting ZnCoO ($\varepsilon_r \geq 13.0$) and ZnMnO ($\varepsilon_r \geq 25.8$) in comparison to unmagnetic ZnO ($\varepsilon_r = 8.3-9.3$) is related to the electrical polarizability of donor-type bound magnetic polarons (BMP) in the several hundred GHz range (120 GHz for CdMnTe). The formation of donor-BMP is enabled in n-type conducting, magnetic ZnO by the s-d exchange interaction between the electron spin of positively charged oxygen vacancies $V^+_o$ in the BMP center and the electron spins of substitutional Mn2+ and Co3+ ions in ZnMnO and ZnCoO, respectively. The BMP radius scales with the Bohr radius which is proportional to the static dielectric constant. Here we show how BMP overlap can be realized in magnetic n-ZnO by increasing its static dielectric constant and guide researchers in the field of transparent spintronics towards ferromagnetism in magnetic, n-ZnO.

The favourable electrical and optical properties of zinc oxide made it promising for applications in opto-electronics1, sensor technology2, UV light emitting diodes3, and photovoltaic devices. In the field of spintronics, special attention has been given to oxygen-deficient magnetic ZnO thin films with substitutional 3d transition metal ions4-6. Observed spontaneous magnetization has been related with the formation of stable Bound Magnetic polarons (BMP)7. The BMP concept was first introduced to explain metal-insulator transition in oxygen-deficient EuO8. BMPs are formed by the s-d exchange interactions between the electron spin of a singly charged oxygen vacancy $V^+_o$ in the center of the BMP and the electron spins of substitutional 3d transition metal ions in a sphere with Bohr radius $r_B$8. The Bohr radius is proportional to the static dielectric constant. Due to the s-d exchange interaction between the spin of singly charged oxygen vacancy $V^+_o$ and the spins of the 3d transition metal ions in the sphere with Bohr radius $r_B$, the spins of the 3d transition metal ions align in same direction and sum up to the collective spin of the BMP. For example, spontaneous magnetization due to collective spins of BMPs in CdTe with substitutional Mn ions was reported by Peter and Eucharista12. From magnetic n-CdS13,14 and n-CdSe15,16 there is abundant evidence that the electron localized at the impurity in the BMP center can induce sizable magnetization in its vicinity, often having magnetic moments exceeding 25 $\mu_B$. Interestingly, so far the focus in the BMP research was more on the formation of BMP and not on the increase of the static dielectric constant in the dilute magnetic semiconductor in comparison to the semiconductor host without substitutional magnetic ions. For example, the static dielectric constant of ZnO amounts to 8.5–9.518–20 and we have observed an increase of the static dielectric constant of ZnCoO up to 25.0 if 4 at.% Co is added1. Investigations of dielectric constant of ZnCoO powders modelled from measured shift in bandgap showed that it is not possible to achieve significant increase in dielectric constant. This may be due to the absence of singly ionised oxygen

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vacancies ($V_o^-$) in ZnCoO powders enabling $s$-$d$ exchange interaction and bound magnetic polaron formation which would enhance the static dielectric constant of ZnCoO powders. In this work we determine the magnetic species and concentration dependent static dielectric constant $\varepsilon_r$ of two ZnO thin films and eight magnetic ZnO thin films with 2 at.% and 5 at.% substitutional Co$^{2+}$ and Mn$^{2+}$ ions from analysis of capacitive metal/n-ZnO semiconductor/Si$_N$/insulator/p-Si semiconductor (MSIS) structures. The oxygen partial pressure during growth of the magnetic n-ZnO films by pulsed laser deposition (PLD) mainly determines the concentration of oxygen vacancies which are intrinsic donors and may form the center of BMP in magnetic ZnO. The intrinsic oxygen vacancy defects are donors that can be estimated from room temperature sheet resistance. This work proposes an approach to determine intrinsic defects from measured sheet resistance and volume of bound magnetic polaron which are the main ingredients that guide researchers towards ferromagnetism in transparent spintronics. The static dielectric constant has been modelled from the measured frequency dependent capacitance characteristics ($C$-$F$) of MSIS structures. The simpler metal insulator metal (MIM) structure for evaluation of static dielectric constant of magnetic, n-type conducting ZnO layers would be problematic for modelling frequency dependent capacitance data. This is because even nominally insulating ZnO thin films in MIM structures are leaky insulators and such MIM structures are not suitable for analysing non-linear frequency dependent impedance. And also, the analysis of current voltage (IV) and impedance (CV) data of Schottky diodes with completely depleted ZnO thin films have too many unknown implicit parameters to extract the static dielectric constant of the ZnO thin film in a Schottky diode from the IV and CV data. Schottky diodes with n-type conducting Zn$_{0.95}$Co$_{0.05}$O thin films have been investigated by Kasper et al.\textsuperscript{7}. Kasper et al. used a static dielectric constant of $\varepsilon_r = 25$\textsuperscript{31}. It was not possible to extract the static dielectric constant of Zn$_{0.95}$Co$_{0.05}$O. Therefore, we chose a MSIS heterostructure in order to extract the static dielectric constant of magnetic, n-type conducting ZnO layers.

**Results**

Oxygen vacancies in n-ZnO are intrinsic donors and increase the concentration of the electron majority charge carriers $n$. If the carrier concentration $n$ is small, the ZnO thin films in the metal/n-ZnO semiconductor/Si$_N$/insulator/p-Si semiconductor MSIS structures are insulating. With decreasing $n$ the carrier mobility $\mu$ increases and influences the dc transport properties of the ZnO in the (MSIS) structures. The ZnO, ZnCoO, and ZnMnO thin films have been grown by PLD on insulator-semiconductor (Si$_N$/p-Si) MIS structures for investigating the static dielectric constant of the magnetic ZnO thin films (Fig. 1). In the following we show how measured impedance has been modelled and how the extracted capacitance of the magnetic ZnO thin films has been used to extract the static dielectric constant of magnetic ZnO in dependence on the species and concentration of magnetic ions. The polarity and strength of the applied bias on the Al/ZnO interface determines the ionization of donor oxygen vacancies ($V_o^-$) (Fig. 1(a–c)). The mobile defects in Si$_N$ are redistributed in Si$_N$ under a bias applied to the MSIS structure, namely with large negative applied bias in accumulation towards the ZnO/Si$_N$ interface (Fig. 1(a)) and for a large positive applied bias inversion towards the Si$_N$/p-Si interface (Fig. 1(c)). The flat band voltage lies in the negative bias range (Fig. S3 in supplementary) for both ramping directions, namely from accumulation (Fig. 1a) to inversion (Fig. 1c) and from inversion to accumulation. This indicates the presence of positive charge defects in Si$_N$ (Fig. S3 in supplementary). Si$_N$ contains both mobile ($\rightarrow$) and fixed ($\uparrow$) positive charge defects. The presence of fixed impurities and mobile positive charge defects in insulating Si$_N$ can be recognized from shift flat band voltage and midgap voltage of conductance and capacitance hysteresis measurements, respectively (Fig. S3). First the distribution of mobile defects in Si$_N$ is changed when the dc bias is ramped from $-15$ V to $15$ V (accumulation in Fig. 1a) or when the dc bias is ramped from $-15$ V to $15$ V (depletion-inversion in Fig. 1bc)). The positive fixed and mobile charge defects in the insulating Si$_N$ layer cause a shift of the flat band voltage to larger negative bias. The mobility of the mobile defects in Si$_N$ depends on the PLD growth temperature during deposition of the n-type semiconductor on the insulator Si$_N$ namely 550°C for the deposition of ZnO in this work and 380°C for the deposition of BiFeO$_3$ in a previous work\textsuperscript{22}. It has been reported that the threshold temperature for the formation of defects in Si$_N$ lies at circa 500°C\textsuperscript{23}.

The small signal analysis of Al/n-ZnO semiconductor/Si$_N$/insulator/p-Si semiconductor structures was performed for obtaining the static dielectric constant of completely depleted ZnO, ZnCoO, and ZnMnO thin films (Fig. 1(c)). The MSIS equivalent circuit model in strong inversion is shown in Fig. 2(b)) and accounts for all RC elements in the interfaces and layers of the MSIS structure. The equivalent circuit model describes the measured nonlinear behaviour of the frequency dependent capacitance (C-F) and conductance (G-F) curve (Fig. S5 in supplementary) of samples grown under different oxygen partial pressures 6.5 × 10$^{-4}$ mbar (LP), 3.91 × 10$^{-4}$ mbar (HP) for two top contact areas A1 ($5.026 \times 10^{-2}$ m$^2$) and A2 ($2.827 \times 10^{-2}$ m$^2$).

The equivalent circuit model describes the impedance characteristics of each region in the MSIS structure that includes each material and the interface regions between the materials. The small signal impedance of MSIS and of MSIS structures is analyzed in strong inversion (s.a. supplementary). An equivalent circuit model describing the frequency dependent capacitance (C-F) and conductance (G-F) of the reference structure, namely of Al/Si$_N$/p-Si/semiconductor (MSIS) structures, is presented in ref. \textsuperscript{24}. In this work we also extended the MOS equivalent circuit model to describe voltage dependent impedance (C-V and G-V)$^{25}$ to the MSIS equivalent circuit model with a n-ZnO semiconductor layer (Fig. 2(b)) (s.a. supplementary). The modelled parameters of the MIS structure (reference samples) have been used as an estimate for the corresponding parameters of the MSIS structures (s.a. S3.1). The modelling of small signal impedance of the MSIS structure always starts in the high frequency range where the leaky Si$_N$ does not dominate frequency dependent small signal impedance (s.a. S3.2). Afterwards the small signal impedance has been modelled in the whole frequency range (s.a. S3.3). $C_{ZnO}$ is the parameter which is finally used to extract the static dielectric constant of the ZnO layer in the MSIS structures.

The equivalent circuit model of the MSIS structure is given in Fig. 2(b). It describes the impedance characteristics of each layer in the MSIS structure and the interface regions between each layer. The capacitor $C$, represents
Figure 1. Schematic representation of charge distribution in the $n$-$ZnO$ layer, the $Si_3N_4$ layer and the $p$-$Si$ in the metal/$n$-$ZnO$ semiconductor/$Si_3N_4$ insulator/$p$-$Si$ semiconductor (MSIS) structure and corresponding band diagram in (a) accumulation (b) depletion and (c) inversion. There are mirror charges on Al top electrode to compensate the charges in $p$-$Si$ accumulated at the interface $Si_3N_4/p$-$Si$. There are singly ionized oxygen vacancies in accumulation and depletion and single and double ionized oxygen vacancies in inversion in ZnO. The majority charge carriers are accumulated at the opposite interface of the ZnO layer. $Si_3N_4$ contains both mobile (•) and fixed (□) positively charged impurities. The existence of the positive impurity charges are expected from the shift of the flat-band voltage towards more negative biases in the negative bias range. Due to the thickness (~110 nm) of the n-type ZnO thin film, only fully depleted or fully accumulated regime band diagram is shown in the figure. Work function of $\Phi_M$ for aluminium metal is 4.3 eV, electron affinity of ZnO $\chi_{ZnO}$ is 4.2 eV, electron affinity of $Si_3N_4$ $\chi$ is 1.8 eV and electron affinity of p-$Si$ $\chi$ is 4.15 eV. Band gap of ZnO $E_{g}^{ZnO}$ is 3.3 eV, band gap of p-$Si$ $E_{g}^{Si}$ is 1.1 eV and bulk potential $\phi_b$ of p-$Si$ is 0.36 eV.
Figure 2. Modelled static dielectric constant of ZnO (•), ZnCoO (◼), and ZnMnO (◇) for top contact area (a) A1 [5.026 × 10⁻⁷ m²] and (c) A2 [2.827 × 10⁻⁷ m²]. The variation of the static dielectric constant which is extracted from $C_{\text{ZnO}}$ used for modelling $[1 \pm (\Delta/2)] \times C_{\text{ZnO}}$ (s.a. error of $C_{\text{ZnO}}$ in Table 1) is indicated as an error bar. Samples grown under low oxygen partial pressure (LP) with $6.50 \times 10^{-3}$ mbar and under high oxygen partial pressure (HP) samples with $3.91 \times 10^{-2}$ mbar are shown in open and closed symbols respectively. (b) Equivalent circuit model for Al/ZnO/Si₃N₄/p-Si/Au MSIS structure at inversion regime (Fig. 1(c)).

Table 1. Modelled static dielectric constant of the ZnO thin films for ZnO_LP, ZnO_HP, Zn₉₈Co₂O_LP, Zn₉₈Co₂O_HP, Zn₉₈Mn₂O_LP, and Zn₉₈Mn₂O_HP from modelled capacitance ($C_{\text{ZnO}}$) and measured SEM thickness (s.a. Supplementary Table S1). The variation of $C_{\text{ZnO}}$ is indicated as an error in Table 1 and the extracted static dielectric constant has an error bar corresponding to the variation of the dielectric constant which is extracted from $C_{\text{ZnO}}$ used for modelling $[1 \pm (\Delta/2)] \times C_{\text{ZnO}}$ in the frequency range from $10^3$ to $6 \times 10^4$ Hz where the capacitance of the whole MSIS structure is most sensitively depending on $C_{\text{ZnO}}$. Conductivity of ZnO thin films have been measured separately with the Hall measurement in van der Pauw geometry. Sheet resistance of ZnO_LP is $1.91 \times 10^2$ ohm/◻, of Zn₉₈Co₂O_LP is $4.55 \times 10^2$ ohm/◻, of Zn₉₈Co₂O_HP is $1.56 \times 10^2$ ohm/◻, and Zn₉₈Mn₂O_LP is $0.09 \times 10^0$ ohm/◻. The free carrier concentration of the ZnO_LP and Zn₉₈Mn₂O_LP is in the range of $10^{12}$ cm⁻³. The free carrier concentration is expected to smaller than the donor concentration because ZnO thin films in the in strong inversion of MSIS structures are completely depleted.

| Sample                  | Conductivity of ZnO | Contact | Thickness of ZnO (nm) | Modelled capacitance (mF/m²) | Dielectric constant |
|-------------------------|---------------------|---------|----------------------|-----------------------------|---------------------|
| ZnO_LP                  | moderate            | A1      | 0.80 ± 0.12          | 08.39 ± 1.25                |
|                         |                     | A2      | 0.89 ± 0.08          | 09.34 ± 0.93                |
| ZnO_HP                  | insulating          | A1      | 0.76 ± 0.04          | 08.87 ± 0.55                |
|                         |                     | A2      | 0.70 ± 0.04          | 08.17 ± 0.48                |
| Zn₉₈Co₂O_LP             | insulating          | A1      | 1.30 ± 0.13          | 17.71 ± 1.77                |
|                         |                     | A2      | 0.96 ± 0.09          | 13.07 ± 1.30                |
| Zn₉₈Co₂O_HP             | insulating          | A1      | 1.12 ± 0.11          | 16.03 ± 1.60                |
|                         |                     | A2      | 0.98 ± 0.09          | 13.09 ± 1.30                |
| Zn₉₈Co₂O_LP             | low                 | A1      | 1.60 ± 0.23          | 21.74 ± 4.34                |
|                         |                     | A2      | 1.62 ± 0.24          | 22.01 ± 3.30                |
| Zn₉₈Co₂O_HP             | low                 | A1      | 1.52 ± 0.23          | 20.31 ± 3.04                |
|                         |                     | A2      | 1.62 ± 0.24          | 21.64 ± 3.24                |
| Zn₉₈Mn₂O_LP             | insulating          | A1      | 2.05 ± 0.20          | 27.00 ± 2.70                |
|                         |                     | A2      | 2.15 ± 0.21          | 28.31 ± 2.83                |
| Zn₉₈Mn₂O_HP             | insulating          | A1      | 1.95 ± 0.30          | 25.83 ± 3.87                |
|                         |                     | A2      | 1.80 ± 0.20          | 27.16 ± 2.71                |
| Zn₉₈Mn₂O_LP             | moderate            | A1      | 2.25 ± 0.35          | 30.49 ± 4.57                |
|                         |                     | A2      | 2.35 ± 0.35          | 31.84 ± 4.77                |
the Si₃N₄ capacitance. The p-Si region consists of p-Si depletion capacitance \( C_{\text{dep}} \) in series with the Si₃N₄ capacitor. The sharp termination of p-Si at the Si₃N₄/p-Si interface causes formation of surface states in p-Si. Those surface states are occupied during strong inversion. The MSIS equivalent circuit model accounts for slow and fast surface states with capacitance/resistance \( C_{\text{fss}}/R_{\text{fss}} \), and \( C_{\text{zss}}/R_{\text{zss}} \), respectively, in parallel to the p-Si depletion capacitance \( C_{\text{dep}} \). The series resistance \( R_{\text{s}} \) includes resistances from undepleted p-Si in series with top electrode and bottom electrode. The bottom contact capacitance \( C_{\text{b}} \) in parallel with the resistor \( R_{\text{b}} \) in the circuit model emulates the Schottky junction between the bottom gold contact and semiconductor. The barrier height calculated from the modelled capacitance of bottom contact agrees with the calculation of barrier height from difference in work function of gold (4.8 eV) and work function of Si (5.07 eV). The sharp interface between ZnO and Si₃N₄ causes the formation of surface states in ZnO at the ZnO/Si₃N₄ interface. The MSIS equivalent circuit model (Fig. 2(b)) also accounts for the slow and fast surface states in ZnO with capacitance/resistance \( C_{\text{fss}}/R_{\text{fss}} \) and \( C_{\text{zss}}/R_{\text{zss}} \) in parallel with the depletion capacitance \( C_{\text{zss}} \) in ZnO, respectively. Also, charges at the interface of top contact aluminum (Al) and ZnO are taken into account with capacitance \( C_{\text{al}} \) in parallel with the resistance \( R_{\text{al}} \). Additional resistive elements \( R_{\text{st}} \) and \( R_{\text{is}} \) (\( R_{\text{st}} = R_{\text{is}} \)) which describe the conductivity changes in the defective Si₃N₄ at the ZnO/Si₃N₄ and Si₃N₄/p-Si interfaces, respectively, have been incorporated into the MSIS equivalent circuit model to describe the defects in the Si₃N₄ (S3.4).

In Fig. 2, dotted vertical lines indicate the interface between each layer. We show arrows at the interface position of ZnO/Si₃N₄ and Si₃N₄/p-Si to sketch that \( R_{\text{st}} \) and \( R_{\text{is}} \) in parallel with the resistance \( R_{\text{is}} \) are finite and belong to the leaky Si₃N₄ dielectric. We see a frequency dependent capacitance for Si₃N₄ in small signal ac analysis. Also, a voltage dependent dc conduction is seen in leaky Si₃N₄. Therefore, Si₃N₄ can be considered as a broken ac channel with same dc conduction and for small signal equivalent circuit. Analytically we considered a capacitor with reduction in effective thickness described by Beaumont and Jacobs model. Because ac conduction does not go through the Si₃N₄ at all frequencies and because of charge neutrality, the resistance change due to accumulation of charges at the interface ZnO/Si₃N₄ (\( R_{\text{st}} \)) and at the interface Si₃N₄/p-Si (\( R_{\text{is}} \)) the corresponding resistance change is the same, i.e. \( R_{\text{st}} = R_{\text{is}} \).

### Discussion

The dielectric constant of the ZnO layer in the MSIS structure has been determined from the modelled \( C_{\text{ZnO}} \) (Fig. 2(b)) using the area of the Al top contacts and the ZnO thickness from SEM measurements (Table S1 in supplementary). The static dielectric constant \( \varepsilon_r \), (Table 1) calculated for ZnO, ZnCoO, and ZnMnO grown at 6.50 ± 10⁻³ mbar (LP), 3.91 ± 10⁻² mbar (HP) oxygen partial pressure is plotted in Fig. 2(a) for contact area A1 and in Fig. 2(c) for contact area A2 (\( A1 = 5.026 \times 10^{-7} \text{ m}^2 \) and \( A2 = 2.827 \times 10^{-7} \text{ m}^2 \)). The modelled static dielectric constant of ZnO ranges between 8.2 and 9.3 and is in good agreement with literature values in the range between 8.5 and 9.5. A strongly increased static dielectric constant has been deduced from \( C_{\text{ZnO}} \) of MSIS structures with ZnCoO and ZnMnO thin films. We also see a slight increase of dielectric constant for ZnO LP and ZnO HP in comparison to bulk ZnO. However, it is not proven so far that the observed increase of dielectric constant in ZnO can be related with magnetism in ZnO, e.g. with magnetism due to the formation of bound magnetic polaron (BMPs). One could speculate that for ZnO LP which has been grown at low oxygen partial pressure and which has a larger concentration of intrinsic donors, more donors are available as centres for BMPs. One possible type of ferromagnetic s-d exchange interaction in pure ZnO is the s-d exchange interaction between 3d electrons of Zn ions and electron spin of oxygen vacancies (Vo⁺). Therefore, we expect an increased volume of bound magnetic polarons (Eq. (1)) in magnetic ZnO in comparison to unmagnetic ZnO.

The resistance of the ZnO has been measured and the transport properties are classified by ranges of resistance in Table 1. Insulating ZnO thin films have lower \( \varepsilon_r \), while low conducting ZnO and moderate conducting ZnO thin films have higher \( \varepsilon_r \), which is an indication of the dielectric constant dependence on donor concentration.

Here the donors are intrinsic donors formed in ZnO by oxygen vacancies (Vo⁺) which concentration depends on the oxygen partial pressure during PLD growth of ZnO. One might expect smaller dielectric constant in higher pressure (HP) samples in comparison to lower pressure (LP) samples, because electrically polarizable BMP represent a collective spin of 3d spins of Mn⁺⁺ in ZnMnO and of Co⁺⁺ spins in ZnCoO which is mediated by s-d exchange interaction between 3d wavefunction of 3d spins and s wavefunction of the electron spin of Vo⁺ in the centre of the bound magnetic polaron (Vo⁺). More BMPs are expected for a larger number of oxygen vacancies in lower pressure samples.

There exist three types of known native donors in ZnO oxide, i.e., O vacancies (Vo⁺), Zn interstitials (IZn⁺), and H related defects (H⁻) which play crucial roles in determining the transport and optical properties of zinc oxide. We investigated the species of shallow donors in ZnO thin films grown by pulsed laser deposition by assuming two different donors with two thermal activation energies in the ZnO. For example, in our previous work Vegesna et al., the existence of two different donors could be proven by modeling the temperature dependent free carrier concentration. This thermal activation energy hints towards hydrogen related defects and zinc interstitials. Because the thermal activation energy of oxygen vacancies amounts to 300 meV Hofmann et al., it is not possible to prove existence of oxygen vacancies in ZnO by temperature dependent transport measurements. Hoffman et al. used photoluminescence measurements and related the green emission from ZnO with the existence of oxygen vacancies. In a recent work Liu et al. showed that oxygen vacancies are the dominant defects in n-type conducting ZnO using oxygen isotope diffusion which depends on the concentration of oxygen vacancies. Here we focus on native point defects providing a single electron spin for the formation of BMP in magnetic, intrinsically n-type conducting ZnO. The only native donor in n-ZnO carrying a single electron spin is the O vacancy (Vo⁺). Zinc interstitials occur exclusively in the 2⁺ charge state, i.e., \( I_{\text{Zn}}^{2⁺} \). Therefore, formation of bound magnetic polarons with \( I_{\text{Zn}}^{2⁺} \) (no electron, \( S = 0 \)), \( I_{\text{O}} \) (paired electrons, \( S = 0 \)) and \( H_{\text{Zn}} \) (no electrons, \( S = 0 \)) is not possible. Only singly ionised oxygen vacancy (Vo⁺) (single electron, \( S = 1/2 \)) can...
form the center of BMP. $V_0^*$ (paired electrons, $S = 0$) and $V_0^{2+}$ (no electron, $S = 0$) with zero-valued electron spin cannot be the center of the donor-BMP.

The spin interaction volume in BMP constitutes a collective spin of 3d spins of $\text{Mn}^{2+}$ and $\text{Co}^{3+}$ which is mediated by s-d exchange interaction between 3d wavefunction of 3d spins and s wavefunction of the spin of $V_0^*$. The volume of bound magnetic polaron defined by the Bohr radius is proportional to the static dielectric constant. The Bohr radius can be calculated using following equation

$$r_b = \frac{4\pi\varepsilon_0\varepsilon_r\hbar}{me^2},$$

where $\varepsilon_0$ is permittivity of free space, $\hbar$ is reduced Planck’s constant, $\varepsilon_r$ is static dielectric constant, $m$ is effective mass ($0.24m_e$) and $e$ is elementary charge.

The bound magnetic polaron (BMP) in ZnCoO and in ZnMnO has a huge collective spin, if many 3d ions lie in the volume of the bound magnetic polaron. The larger the number of 3d ions in the BMP volume, the more spins of 3d ions can be aligned in parallel by the s-d exchange between the spin of the oxygen vacancy ($V_0^*$) in the center of the BMP and the spins of the 3d ions in the BMP volume within the Bohr radius $r_H$. The BMP will increase the polarizability of magnetic ZnO.

In our work, we have extracted the static dielectric constant from frequency dependent impedance data measured on ZnO coated MSIS structures. The model does not capture frequency dependence of the dielectric constant of ZnO. In the measured frequency region up to 1 MHz the dielectric constant of ZnO is expected to be constant. Therefore, a time dependent switching characteristics of static dielectric constant in ZnO can only be studied if the switching is non-volatile. For example, the model could possibly be used to investigate the dynamics of spin alignment in BMPs in magnetic, n-ZnO if single magnetic field pulses of different lengths are applied before the measurement of impedance data in dependence on the magnetic field pulse length. Before applying subsequent magnetic field pulse and before measuring the resulting frequency dependent impedance data, the spin alignment in the BMP has to be destroyed, e.g. by an ac magnetic field. We expect that the dynamics of the spin alignment in BMPs will depend on the volume and on the material dependent ferromagnetic s-d exchange parameter. A direct measurement of the spin dynamics in BMP would be possible if the frequency dependence of the dielectric constant could be measured in the several hundred GHz frequency range, e.g. by microwave measurements.

In the following we discuss possible percolation of BMP in ZnO with dependence on the static dielectric constant and the concentration of oxygen vacancies. Coey and Venkatesan estimated the concentration of defects in ZnO for polaron percolation based on a static dielectric constant of ZnO of $\varepsilon_r$ and Bohr radius ($r_b$). A threshold concentration of defects in ZnO of $4 \times 10^{19}$ cm$^{-3}$ has been obtained for $\varepsilon_r = 4.0$ and $r_b = 0.76$ nm from $(n_{\text{crit}}^{\text{ZnO}})^{1/3}$ $r_b \approx 0.26$, where $n_{crit}^{ZnO}$ is the critical defect concentration for delocalization of the impurity band states. In Fig. 3 we show the calculated BMP diameter in ZnO thin films with different static dielectric constants ($\varepsilon_r(A1) = 8.39$ (ZnO LP), 17.71 (Zn$_{99.5}$Co$_{0.5}$O LP), 21.74 (Zn$_{99.5}$Co$_{0.5}$O LP), 27.00 (Zn$_{99.5}$Mn$_{0.5}$O LP), and 30.49 (Zn$_{99.5}$Mn$_{0.5}$O LP)) and with the density of oxygen vacancies ranging from $10^{16}$ cm$^{-3}$ to $10^{22}$ cm$^{-3}$. For simplicity, for the determination of the distance between oxygen vacancies we have considered a homogeneous oxygen vacancy distribution. The diagonal black solid line gives the distance between two oxygen vacancies in dependence on concentration of oxygen vacancies. If the distance between the oxygen vacancies is smaller than the diameter of BMP, BMPs coalesce and overlap. Such overlap of bound magnetic polarons possibly induces
ferromagnetism in magnetic ZnO at room temperature if the orientation of the electron spin of the oxygen vacancy in the center of BMP is stable and not continuously changing due to hopping transport of free carriers via oxygen vacancies.

We describe the frequency dependent capacitance (C-F) behaviour of the AlInn-ZnO semiconductor/SiN4 insulator/p-Si semiconductor MSIS structure with an equivalent circuit model in strong inversion regime where each layer and interface has been described. Static dielectric constant of ZnO has been extracted from modelled capacitance of the ZnO layer. The dielectric constant of ZnO lies in the expected range from 8.1 to 9.3. We observed strongly increased static dielectric constant in magnetic ZnO in dependence on the concentration of magnetic ions and on the concentration of oxygen vacancies. The dielectric constant in ZnMnO with 5 at. % Mn is 28.3 and with 2 at. % Mn is 31.8. The dielectric constant in ZnCoO with 5 at. % Co is 17.7 and with 2 at. % Co is 22.0. The ferromagnetic s-d exchange interaction between electron spin of donors (V_\text{\textsc{d}}^+) in the center of the bound magnetic polaron (BMP) and the electron spin of substitutional magnetic ions is partially superimposed by the anti-ferromagnetic coupling between nearest neighbours substitutional magnetic ions. With increasing concentration of substitutional magnetic ions it is expected that the anti-ferromagnetic coupling which excludes ferromagnetic s-d coupling increases and weakens the formation of BMPs. This is the possible reason why we see a larger static dielectric constant in magnetic ZnO with 2 at. % substitutional magnetic ions in comparison to magnetic ZnO with 5 at. % substitutional magnetic ions. The observed trend is in agreement with the observations from Franco et al. on powdered ZnCoO who observed a maximum of static dielectric constant in powdered ZnCoO around 2 at. % Co. We related the increased static dielectric constant in magnetic ZnO with the formation of partially overlapping bound magnetic polarons and their contribution to the electrical polarizability of magnetic ZnO.

Finally, we estimated the contribution of the BMP in ZnO to the polarizability of ZnO. The resonance of BMP typically lies in the several hundred GHz range. Here we chose the same resonance of BMP in magnetic ZnO as shown for the magnetic semiconductor CdMnTe where an additional absorption due to BMP has been observed at 120 GHz by Raman shift measurements (4 cm^{-1})^{42}. We assumed an additional polarizability of magnetic ZnO due to BMP and added this to the modelled imaginary part (\epsilon_2) of the dielectric constant (Fig. 4(b,d,f)).

\[
\epsilon_2(x) = \epsilon_2^{\text{BMP}}(x) + \epsilon_2^{\text{Phonon}}(x) + \epsilon_2^{\text{Electronic}}(x)
\]

(2)

where \epsilon_2^{\text{BMP}} is the contribution due to BMP, \epsilon_2^{\text{Phonon}} is the contribution due to phonons in ZnO^43 and where \epsilon_2^{\text{Electronic}} is the contribution due to electronic transitions in ZnO^{44}. \epsilon_2^{\text{BMP}} has been described with a Lorentz oscillator model as follows:

\[
\epsilon_2 = 1 + N_{\text{peak}} \left( \frac{\Gamma\omega}{\omega_0^2 - \omega^2 + i\Gamma\omega} \right) + \Gamma^2\omega^2
\]

(3)

where \omega_0 is the BMP peak position (\omega_0=120 GHz), N_{\text{peak}} is the peak strength and \Gamma is the FWHM. We calculated the real part (\epsilon_1) of the dielectric constant (Fig. 4(a)) using Kramers-Kronig relation (Eq. (4)) for ZnO with the electronic and phonon contribution to \epsilon_2. Additionally, the FWHM of a Lorentz oscillator with a fixed peak strength (N_{\text{peak}} = 350) and fixed peak position has been varied to change the contribution from \epsilon_2^{\text{BMP}} to \epsilon_2 in Fig. 4(d,f) and derived \epsilon_2 of magnetic ZnO in Fig. 4(e), respectively, using Kramers-Kronig relation (Eq. (4)) \epsilon_2^{\text{BMP}} as long as static dielectric constant \epsilon_1 from Eq. (4) was the same as the modelled static dielectric constant from impedance measurements (\epsilon_2).

\[
\epsilon_1(\omega) = \epsilon_\infty + \frac{2}{\Pi} \int_0^{\infty} x \cdot \epsilon_2(x) \frac{dx}{x^2 - \omega^2}
\]

(4)

Estimated FWHM for Zn_{0.95}Co_{0.05}O is \Gamma = 0.7 GHz, Zn_{0.85}Mn_{0.15}O is \Gamma = 1.41 GHz, Zn_{0.99}Co_{0.01}O is \Gamma = 0.8 GHz, and Zn_{0.95}Mn_{0.05}O is \Gamma = 6.1 GHz.

We expect that the dielectric constant peak position can be tuned via the material dependent ferromagnetic s-d exchange parameter. Here we rather focused on the amplitude of the additional absorption \epsilon_2^{\text{BMP}} in the several hundred GHz range. We expect that the amplitude can be tuned via the volume of the interface region between materials. Dielectric constant is obtained from modelled ZnO capacitance value and with the thickness of ZnO from SEM measurements. Dielectric constant for ZnO is obtained in the expected range \epsilon_2 = 8.17–9.34. We determined the static dielectric constant in magnetic, n-type conducting ZnO thin films with different Co and Mn concentration. With 2 at. % it is 31.84 and for 5 at. % Mn sample dielectric constant is 28.31 and for 2 at. % Co samples dielectric constant is 22.31 and for 5 at. % Co sample it is 17.71. We attribute the increase of the static dielectric constant to the contribution of bound magnetic polarons to the electrical polarization of magnetic, n-type conducting ZnO.
Figure 4. Real part ($\varepsilon_1$) of dielectric constant for (a) ZnO, (c) Zn$_{0.95}$Co$_{0.05}$O, Zn$_{0.95}$Mn$_{0.05}$O, and (e) Zn$_{0.98}$Co$_{0.02}$O, Zn$_{0.98}$Mn$_{0.02}$O has been estimated by applying Kramers-Kronig transformation to imaginary part ($\varepsilon_2$) of dielectric constant for (b) ZnO, (d) Zn$_{0.95}$Co$_{0.05}$O, Zn$_{0.95}$Mn$_{0.05}$O, and (f) Zn$_{0.98}$Co$_{0.02}$O, Zn$_{0.98}$Mn$_{0.02}$O, respectively. The electronic and phonon contribution to $\varepsilon_2$ has been taken from literature. An additional contribution to $\varepsilon_2$ due to BMP at 120 GHz has been assumed in such a way that $\varepsilon_1$ agrees with modelled $\varepsilon_r$. 
With increase in oxygen vacancies at the surface, bound magnetic polaron formed with oxygen vacancy as nucleus can overlap and provide ferromagnetic behaviour at room temperature\(^\text{15}\) Davies et al.\(^\text{15}\) and Kaspar et al.\(^\text{7}\) suggest that ferromagnetic features from bound magnetic polaron can be used in developing magnetic sensors, non-volatile memories in spintronics devices which are potentially expected to be energy-efficient devices. Application of BFO coated \(\text{Si}_3\text{N}_4\) MIS structure as a photocapacitive detector has been studied by You et al.\(^\text{22}\).

Because \(\text{ZnO}\) is transparent and because the \(\text{ZnO}\) coated \(\text{Si}_3\text{N}_4\) MIS structure shows similar capacitance behaviour as the BFO coated \(\text{Si}_3\text{N}_4\) MIS structure, the \(\text{ZnO}\) coated \(\text{Si}_3\text{N}_4\) MIS structure is expected to reveal similar photocapacitive functionality as the BFO coated \(\text{Si}_3\text{N}_4\) MIS structure to detect intensity and color of visible light by impedance measurements. In addition, we suggest to use the \(\text{ZnO}\) coated \(\text{Si}_3\text{N}_4\) MIS capacitor as magnetoe-capacitive detector where the presence of a magnetic field can be detected via the increase of static dielectric constant due to the formation of BMPs with aligned spins of magnetic ions.

We propose to study change of static dielectric constant in magnetic transparent conducting oxides (TCO)\(^\text{47,48}\) by preparing metal/\(n\)-TCO/insulator/\(p\)-Si MSIS structures and by measuring and modelling the impedance in strong inversion. It is expected that also other magnetic \(n\)-type conducting TCOs reveal an increase of static dielectric constant due to the formation of bound magnetic polarons and due to the contribution of BMP to the polarizability of magnetic TCOs. Bound magnetic polarons strongly influence transport, magnetization and magnetooptical properties in magnetic semiconductors within the confined volume of BMPs. For example, ferromagnetic behaviour in magnetic \(\text{ZnO}\) at room temperature can be related with BMP\(^\text{40,41}\) and it has been suggested that ferromagnetic behavior related with BMP formation in magnetic \(n\)-type conducting TCOs can be used in developing magnetic sensors and non-volatile memories in spintronics devices with a low energy consumption\(^\text{29}\). If BMPs are coalescing, even at the room temperature strongest effect of BMPs on the transport, magnetization and magnetooptical properties\(^\text{3}\) of magnetic semiconductors can be expected.

### Methods

First alpha silicon nitride (\(\alpha\)-\(\text{Si}_3\text{N}_4\)) thin films with a nominal thickness of about 88 nm were deposited in a Roth and \(\text{R}\) \& \(\text{A}\) AK1000 microwave PECVD reaction chamber. Afterwards \(\text{ZnO}\), \(\text{ZnCoO}\), and \(\text{ZnMnO}\) thin films with the nominal concentration of 2 at.% and 5 at.% \(\text{Co}\) and \(\text{Mn}\) have been grown on top of \(\text{Si}_3\text{N}_4/p\)-MSIS structures by PLD with 700 1 Hz \(\text{KrF}\) excimer laser pulses with energy density of 1.60 \(\text{J/cm}^2\) to ablate \(\text{ZnO}\), \(\text{ZnMnO}\), and \(\text{ZnCoO}\) ceramic targets at a substrate temperature of 550 °C with a constant oxygen flux of 4.50 sccm. Two different oxygen partial pressures, 6.50 \(\times\) 10\(^{-3}\) mbar and 3.91 \(\times\) 10\(^{-2}\) mbar, have been applied to control the concentration of oxygen vacancies in the magnetic \(\text{ZnO}\) thin films. The bottom of the \(p\)-Si has been coated with gold (\(\text{Au}\)) using \(dc\) magnetron sputtering at room temperature to form a bottom contact to the MIS structure. Circular \(dc\) magnetron sputtered aluminium dots of different size have been prepared on the \(\text{ZnO}\) films to form the top contacts on the MIS structure. For impedance measurements we have chosen \(Al\) contacts with and area of 5.026 \(\times\) 10\(^{-2}\) \(\text{m}^2\) (\(Al\)1) and of 2.827 \(\times\) 10\(^{-2}\) \(\text{m}^2\) (\(Al\)2).

Structural properties of investigated ten different metal/\(n\)-\(\text{ZnO}\) semiconductor/\(\text{Si}_3\text{N}_4/\text{Si}_3\text{N}_4\) insulator/\(p\)-Si semiconductor (MSIS) structures, mainly thickness of the \(n\)-\(\text{ZnO}\) and \(\text{Si}_3\text{N}_4\), have been determined using secondary electron microscopy (SEM) cross section measurements (Sect. S1). Impedance of the MSIS structures with ten different \(\text{ZnO}\), \(\text{ZnCoO}\), and \(\text{ZnMnO}\) thin films grown on \(\text{Si}_3\text{N}_4/p\)-Si was measured versus voltage (\(V\)) and versus frequency (\(F\)) using the Agilent 4294A precision impedance analyzer. We determined the bias range for the different regimes in the MSIS structure (accumulation, depletion, inversion, strong inversion) by voltage dependent impedance measurements (Sect. S2). Nonlinear behaviour of the frequency dependent capacitance (\(C-F\)) and conductance (\(G-F\)) of all MSIS structure in strong inversion has been modelled with an equivalent circuit model which accounts for all RC elements in the interfaces and layers of the MSIS structure. The static dielectric constant of \(n\)-\(\text{ZnO}\) has been extracted from modelled capacitance (\(C_{ZnO}\)) of completely depleted \(n\)-\(\text{ZnO}\) layer of the MSIS structure (Sect. S3).

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Sahitya V. Vegesna and Prof. Dr. Heidemarie Schmidt wrote the main manuscript text and Vinayak J. Bhat prepared all figures. Ilona Skorupa deposited and prepared the samples. Dr. Danilo Bürger was responsible for the characterization of transport properties with Hall measurements. Scanning electron microscopy measurements were performed by Dr. Jan Dellith. Prof. Dr. Oliver G. Schmidt and Prof. Dr. Heidemarie Schmidt discussed the main ideas of the paper.

Competing interests
The authors declare no competing interests.

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