Colossal Spin Hall Effect in Ultrathin Metallic Films

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We predict spin Hall angles up to 80% for ultrathin noble metal films with substitutional Bi impurities. The colossal spin Hall effect is caused by enhancement of the spin Hall conductivity in reduced sample dimension and a strong reduction of the charge conductivity by resonant impurity scattering. These findings can be exploited to create materials with high efficiency of charge to spin current conversion by strain engineering.

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An efficient transformation of charge into spin current is the key issue for future applications of the spin Hall effect (SHE) in spintronic devices. The figure of merit for this phenomenon is described by the spin Hall angle (SHA). For a long time, its largest value was 11% measured in Au [3]. Subsequently, several studies revealed systems that provide SHAs of comparable magnitude, the so-called giant SHE [3]. Among them, a SHA of −12% to −15% was measured in highly resistive β-Ta [4]. Even larger values of 30% to 33% were obtained by an experimental study of β-W thin films [5]. Both results have been qualitatively predicted evaluating a tight-binding model [3]. In addition, a SHA of −24% has been reported for thin film Cu(Bi) alloys [6]. The large magnitude of the SHA for a copper crystal with Bi impurities was predicted by first-principles calculations relying on the skew-scattering mechanism [8]. The existing results inspire both theorists and experimentalists to search for new routes to synthesize materials with even larger SHAs.

In this Letter we show that the SHA caused by impurities in ultrathin metallic films can reach values up to 80%. We concentrate on the skew scattering as the responsible mechanism for the SHE in dilute alloys [3,11]. The results are based on ab initio calculations developed originally for bulk crystals [3] and later extended to the case of two-dimensional (2D) systems [11]. The parameter we are going to optimize is the spin Hall angle

\[ \alpha = \frac{\sigma_{yx}^s}{\sigma_{xx}} \quad (1) \]

defined as the ratio of the spin Hall conductivity (SHC) \( \sigma_{yx}^s \) to the longitudinal charge conductivity \( \sigma_{xx} \). This ratio is dimensionless since both conductivities are expressed in the same units [3,11,12]. For the skew-scattering mechanism both depend inversely on the impurity concentration which provides a concentration independent. Consequently, this quantity is ideally suited for comparison with experiment.

In our previous study [11] we showed that the SHE induced by Pt impurities in Au(111) films can be significantly enhanced for a reduced film thickness. Especially for the one monolayer (ML) films a large SHA of −13% to −18% was obtained for the case of Pt adatoms [11]. For these systems the origin of the giant SHE was related to the enhanced effective spin-orbit coupling (SOC) induced by the reduced coordination number and the associated strong potential gradients. In combination with a single-sheeted Fermi surface it leads to the mentioned strong effects. On the other hand, substitutional Bi impurities in bulk Cu provide a giant SHE as well. In this case the large valence difference between impurity and host atoms causes strong scattering as well as strong effective SOC. The idea of this paper is to combine both facts and screen the influence of Bi impurities in ultrathin noble metal films. Accordingly, we focus on the 1 ML films considering Bi as adatom or substitutional impurity. Figure 1 shows the general setup for our calculations.

![FIG. 1: (Color online) Geometry of the considered systems shown for a freestanding 1 ML fcc (111) film with an adatom (left) or a substitutional impurity (right).](image)

The corresponding results obtained by the approach of Ref. [11] are presented in Fig. 2 where the SHA, the SHC, and the charge conductivity are shown for 1 ML (111) and (001) noble metal films. Throughout the paper, the impurity density chosen for the films corresponds to 1 at.% impurity concentration used for the bulk crystals. First, nearly all values of the SHA shown in Fig. 2 (a)-(b) are drastically increased in comparison to the related bulk systems with \( \alpha < 10\% \) [3]. The SHAs for the (111) films are even larger than the values reported in Ref. [11] for the corresponding hosts with Pt impurities (\( \alpha < 19\% \)). Thus, combining the reduced coordination number of the impurity with the large valence difference between impurity and host atoms seems to be a proper way to enlarge the SHA. In detail, the enhancement of

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FIG. 2: (Color online) The spin Hall angle $\alpha$, the spin Hall conductivity $\sigma_{yx}^s$, and the charge conductivity $\sigma_{xx}$ for 1 ML (111) and (001) Cu, Ag, and Au films with Bi as adatoms (blue rings) and substitutional impurities (red filled disks). For comparison, the corresponding bulk values [13] are shown with black diamonds. The conductivities are given in units of $\mu\Omega\text{cm}^{-1}$ while $\alpha$ is shown in percent.

FIG. 3: (Color online) The results of transport calculations performed at different energies around the Fermi level ($E_F$) are shown for 1 ML (111) and (001) Cu, Ag, and Au films with substitutional Bi impurities. The corresponding $\alpha$ (red filled disks), $\sigma_{yx}^s$ (blue diamonds), and $\sigma_{xx}$ (green squares) are displayed and $\alpha(E_F)$ is highlighted with a larger disk. All quantities have absolute values in the same order of magnitude but different units: the conductivities are in $\mu\Omega\text{cm}^{-1}$ while $\alpha$ is dimensionless and has to be multiplied by 100 to get the values in percent.

The SHA in comparison to the bulk results is solely determined by the SHC which is strongly increased in all systems, as shown in Fig. 2 (c)-(d). By contrast, the charge conductivity alone would cause a reduction of $\alpha$, since it is also increased in comparison to the bulk values but enters Eq. [1] in the denominator.

Another striking feature is the strong dependence of the SHA on the host material for substitutional Bi impurities in (111) films, culminating in the 80% value for Au. In contrast to the other configurations, $\sigma_{yx}^s$ and $\sigma_{xx}$ change for this case in opposite direction going from Cu via Ag to Au, see Fig. 2 (c) and (e). As a result, both conductivities facilitate to amplify the corresponding SHA shown in Fig. 2(a). However, the influence of the charge conductivity is stronger. Within the (111) films $\sigma_{xx}$ is reduced by a factor of 4 changing the host from Cu to Au. The particularly small charge conductivity of Au(111) films with substitutional Bi impurities finally causes the colossal effect. Therefore, the following detailed analysis will focus on substitutional impurities.

In order to get a deeper insight into the underlying mechanism of the colossal SHE, we investigate the energy dependence of the obtained quantities. The corresponding values for the SHA and its constituents, $\sigma_{yx}^s$ and $\sigma_{xx}$, are shown in Fig. 3. In all cases $\alpha$ is strongly energy dependent. Here, it is important to mention that the considered energy interval is so small that the topology of the single-sheeted 2D Fermi surface of the 1 ML films remains unchanged.

Analyzing the contributions to the SHA from the charge and spin Hall conductivity separately, one can see differences depending on the host material. While for Au the energy dependence of $\alpha$ is almost solely determined by the charge conductivity, $\sigma_{yx}^s$ and $\sigma_{xx}$ play
a comparable role for Cu and Ag. Nevertheless, a certain correlation between the two conductivities exists for all considered systems. Namely, the SHC increases with decreasing charge conductivity and vice versa, which is most obvious for the Ag films. This is related to the fact that, generally, stronger scattering should reduce $\sigma_{xx}$ but enhance $\sigma_{yx}$ \cite{11}. However, the situation in real systems can differ from such a simplified picture. For instance, the pronounced maximum of the SHA in the Au films is merely determined by the corresponding minimum of the charge conductivity. For both (111) and (001) Au films small changes of energy strongly affect $\sigma_{xx}$ while $\sigma_{yx}$ remains almost constant. In the case of the 1 ML Au(111) film the minimum of the charge conductivity occurs in the vicinity of the Fermi level $E_F$, which causes the colossal SHA shown in Fig. 2(a). Thus, going from bulk Au to the 1 ML Au(111) film, the giant SHE occurs since the SHC is increased due to enhancement of the SOC and the absence of interband scattering \cite{11}. Finally, the SHA is further enhanced through the suppression of the charge conductivity. These are the ingredients of the reported colossal SHA.

The origin of the reduced charge conductivity is resonant scattering, as demonstrated in Fig. 3, presenting the impurity local density of states (LDOS). Bi impurities are known to be strong $p$-scatterers \cite{7,8,12}. Because of SOC the $p$-level is split into $p_{1/2}$ and $p_{3/2}$. The minimum of the charge conductivity is obviously correlated with the maximum of the $p_{1/2}$ LDOS of the Bi impurity (Fig. 3).

Although the correlation between the $p_{1/2}$ impurity LDOS and the charge conductivity is obvious, the underlying mechanism is quite complex. As shown in the Supplemental Material \cite{14}, for all considered systems the vertex corrections are of utmost importance for the energy dependence of $\sigma_{xx}$. Being also the source of the considered skew-scattering contribution to the SHC, they occur in the used Boltzmann equation by the so-called scattering-in term \cite{6,11}. This has a very subtle integral structure and is obtained via an iterative procedure within our first-principles calculations \cite{14}. Therefore, it is difficult to provide a simple explanation for the relation between the impurity LDOS and the charge conductivity.

Nevertheless, the strong influence of the vertex corrections is clearly connected to the resonance scattering. Indeed, the well-pronounced peaks of the impurity LDOS near $E_F$, shown in Fig. 3, are missing in the case of substitutional Bi atoms in bulk Au \cite{14} and Cu \cite{14}. As a consequence, the energy dependence of the charge conductivity for bulk crystals is practically unaffected by the scattering-in term \cite{14}.

With this microscopic picture in mind, it is possible to understand the host dependence of $\alpha$ for the two surface orientations. As illustrated by Fig. 3 the general energy dependence $\alpha(E)$ is extremely similar between (001) and (111) films for each host material. However, in the (001) case the reduced coordination number causes a smaller charge density. As a result, the related impurity resonance is shifted to higher energies with respect to the Fermi level. The conductivity minimum is shifted accordingly. In addition, strong changes of $\sigma_{xx}$ at energies around $E_F$ cause strong variations of $\alpha$. Thus, it is somewhat accidental that the SHA shown in Fig. 2 is nearly the same for the (001) films while it varies strongly for the (111) films. Shifting the Fermi level of the (001) films slightly to higher energies would simulate the situation of the (111) surface orientation.

This finding can be employed to optimize the SHA. The only condition required is to fix the $p_{1/2}$ impurity resonance at the Fermi level. A possible opportunity is strain engineering of the film grown on an appropriate substrate. To prove this assumption, let us choose the Cu(111) film showing the smallest SHA among all the considered systems, as indicated by Fig. 2 (a)-(b). According to Fig. 4 the peak of the corresponding $p_{1/2}$ impurity LDOS is below $E_F$. Following the discussion above, we can assume that an increase of the host lattice constant should provide a shift of the impurity resonance towards the Fermi level. Figure 5 shows that the desired condition can be fulfilled if the lattice constant of Cu is used for the hypothetically strained Cu(111) film. The increase of the lattice constant by about 13% from $a_{\text{Cu}} = 3.615$ Å to $a_{\text{Cu}} = 4.078$ Å shifts the maximum of the $p_{1/2}$ impurity LDOS close to $E_F$. This in return leads to the colossal SHA as shown in the right part of Fig. 4.
FIG. 5: (Color online) Left: The $p_{1/2}$ local density of states at a substitutional Bi impurity atom in 1 ML fcc (111) film of Cu (solid coppery, dark), Au (solid golden, bright), and Cu with the gold lattice constant (dashed brown). Right: The corresponding SHA calculated at $E_F$ for Bi in Cu (circle), Au (square), and Cu with the gold lattice constant (diamond).

Of course, the considered change of the lattice constant is quite strong. Nevertheless, the presented results indicate a new route to design materials with large $\alpha$.

A substrate is needed in general, since the freestanding 1 ML films considered in our study are quite artificial from a practical point of view. To have more realistic systems for observation of the colossal SHE, a possible way is to grow these films on an insulating substrate. However, in such a case the SHE can be modified by the Rashba-type SOC \cite{17}, forcing electron spins to be oriented within the film plane. By contrast, the considered SHE is largest for spins pointing out of plane. In order to ensure the desired spin orientation, a symmetric quantum well structure insulator/metal film/insulator could be utilized.

In summary, we predict a colossal spin Hall effect related to spin Hall angles up to 80%, which are obtained for ultrathin noble metal films with substitutional Bi impurities. This strong effect occurs for systems where the giant SHE, caused by the reduced dimension of samples, is further amplified by a minimal charge conductivity caused by resonant scattering. This condition is achieved if the impurity $p_{1/2}$ resonance state is pinned at the Fermi level. The required resonant scattering can be tuned by strain engineering, depositing films on an appropriate substrate. Our findings offer a new route to design materials with a very efficient conversion of charge current into spin current.

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