THE HALL EFFECT IN HYDRIDED RARE EARTH FILMS:
REMOVING BILAYER EFFECTS

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We describe two new techniques for measuring the Hall effect in capped rare earth films during hydriding. In one, we simultaneously measure resistivity and the Hall coefficient for a rare earth film covered with four different thicknesses of Pd, recovering the charge transport quantities for both materials. In the second technique, we replace Pd with Mn as the covering layer. We will present results from both techniques.

1. Introduction

Palladium overlayers have been used in a number of studies of hydriding in materials.\textsuperscript{1–5}

The Pd overlayer can help stabilize the underlying material during hydriding, preventing it from crumbling into powder during the process. It can also protect the underlying material from corrosion by oxygen after deposition, as would occur for the highly reactive rare earths. Finally, Pd can catalyze the absorption of hydrogen by converting molecular hydrogen into atomic hydrogen, in the case of materials like aluminum,\textsuperscript{4} converting the hydrogen into a form that can be absorbed by the material.

The presence of this overlayer, however, complicates the analysis of charge transport data — resistivity and the Hall coefficient — taken during the hydriding process. For such studies, it becomes necessary to subtract off the effect of the overlayer from the rest of the bilayer.

To determine whether this overlayer significantly alters charge transport in the bilayer, one needs to know how the resistivity and Hall coefficient of the bilayer depend on the charge transport of each layer. The two films behave like two parallel resistors. That is, their inverse resistances, $1/R$, add. In terms of the material properties of the films,

$$ (t\sigma)_{\text{total}} = (t\sigma)_1 + (t\sigma)_2, \quad (1) $$

where $t$ is the thickness, $\sigma$ the conductivity, and the subscripts 1 and 2 refer to the two films. In the presence of a magnetic field, the conductivity becomes a non-diagonal tensor, with all of its components behaving as in Eq. (1). This includes the off-diagonal components\textsuperscript{6,7}

$$ (t\sigma_H)_{\text{total}} = (t\sigma_H)_1 + (t\sigma_H)_2 \quad (2) $$

as well, where $\sigma_H$ is the Hall conductivity,

$$ \sigma_H = HR_H\sigma^2, \quad (3) $$

for modest magnetic fields, $H$ (such that the product of $H$, the Hall coefficient, $R_H$, and the conductivity, $\sigma$, is sufficiently small: $HR_H\sigma \ll 1$).

Since the Hall conductivity is inversely proportional to the square of the resistivity, the resistivity of each constituent layer is the most important parameter in determining the composite Hall coefficient of the bilayer. For rare earth films covered with much thinner layers of Pd, the majority of the Hall conduction often takes place within the Pd layer, as shown...
Table 1. Thickness times conductivity (tσ) and thickness times Hall conductivity (tσH) for various metals, compared to a hypothetical palladium overlayer of 20 nm thickness. The relatively large values of these quantities for the Pd overlayer covering the rare earths Gd and Dy suggest that conduction in the bilayer is primarily in the Pd layer: bilayer effects dominate.

<table>
<thead>
<tr>
<th></th>
<th>t</th>
<th>tσ</th>
<th>tσH at 0.6 T</th>
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<tbody>
<tr>
<td></td>
<td>(nm)</td>
<td>(Ω⁻¹)</td>
<td>(10⁻⁵Ω⁻¹)</td>
</tr>
<tr>
<td>Pd</td>
<td>20</td>
<td>0.19</td>
<td>-200</td>
</tr>
<tr>
<td>Ref. 2 Gd</td>
<td>300</td>
<td>0.22</td>
<td>-200</td>
</tr>
<tr>
<td>Ref. 4 Al</td>
<td>50</td>
<td>1.8</td>
<td>-1000</td>
</tr>
<tr>
<td>Ref. 5 Dy</td>
<td>300</td>
<td>0.33</td>
<td>-40</td>
</tr>
</tbody>
</table>

Table 1 shows the product of thickness and conductivity, on one hand, and thickness and Hall conductivity, on the other, for films of various materials studied in Refs. 2, 4 and 5, and a typical 20 nm overlayer of Pd. The Pd alters what one measures for the charge transport properties for thick rare earth films, but has much less impact on the much thinner Al films.

While Eqs. (1)–(2) should, in principle, allow us to subtract out the effects of the Pd overlayer on both resistivity and the Hall coefficient, in practice we are hampered by the fact that these quantities change in the Pd layer during the hydriding process as well as in the material of interest. One way of correcting this situation is to simultaneously measure charge transport in a Pd-capped bilayer and in a single layer of Pd. In practice we can minimize the error in such an approach by simultaneously measuring charge transport in several bilayers in which the material of interest, of a constant thickness, is covered by different thicknesses of Pd.

2. The Step Method
2.1. Description

Figure 1 illustrates how we do just that. A series of bilayers as shown in the figure is deposited on a glass substrate. The material has the form of five connected cross-shaped specimens with a shared central channel. The center of each cross consists of a bilayer of the material of interest covered with a layer of Pd. For the specimen shown in Fig. 1(b), the five specimens consist of a single layer of the underlying metal, three bilayers consisting of the same thickness of that material covered with different thicknesses of the overlayer material, and a single layer of this overlayer material. One can use the van der Pauw technique to measure the resistivity and Hall coefficient of each bilayer.

The charge transport properties of each material can be calculated by a linear fit of film thickness times either the conductivity or the Hall conductivity as a function of the thickness of the covering layer. Extrapolating the data to zero overlayer thickness, we can calculate the conductivity of the underlying material. The slope of the straight-line fit gives the conductivity of the covering layer. A fit of Hall conductivity to overlayer thickness yields similar expressions of the Hall conductivity.

2.2. Experiment

Films were prepared by electron beam deposition on a glass substrate at room temperature at a base pressure of about 10⁻⁶ Torr. After deposition, the specimen was removed from the vacuum chamber and placed in a sample holder in a vacuum chamber inside an electromagnet for charge transport measurements. Hydrogen concentration in the bilayer was monitored with a calibrated quartz crystal microbalance.

In Al:Pd bilayers, the palladium overlayer does not dominate the conduction and Hall conduction of the bilayer. Thus the step method can be accurately
used to remove the effects of the overlayer. We deposited a 50 nm single layer of aluminum; three Al:Pd bilayers of 50 nm Al covered by 5 nm, 10 nm, and 20 nm of Pd; and a single 20 nm layer of Pd. We chose such a thin layer of Al since earlier work showed that Al films have a maximum hydrogen absorption for layers thinner than 60 nm.

Figure 2 shows reasonable agreement between the values for the Al resistivity ratio and Hall ratio calculated with the step method and the values obtained directly from the single layer films of Al. Over the same range of hydrogen concentrations, the Pd layer changes by 7% and 23% respectively (compared to 2% and 7% for Al) in the resistivity and Hall ratio.

This approach works well only if the layer to be studied has sufficiently large values of $t \sigma$ and $t \sigma_H$, relative to the covering layer. For the rare earths covered by thin Pd overlayers, this is not the case, as seen in Table 1. An alternative approach is needed if one chooses to study the rare earths.

### 3. The Alternative Overlayer Method

#### 3.1. Description

The difficulty in the Dy:Pd data is the result of the high conductivity, and thus Hall conductivity, of the covering layer, relative to the rare earths. If we could replace Pd with a material with a much larger resistivity, its impact on the charge transport in the bilayer would be small, and we could simply ignore its presence. On the other hand, such a layer would need to allow hydrogen to pass through it to the layer underneath, while blocking oxygen diffusion. Ideally, it would be a material that dissociates molecular hydrogen into atomic hydrogen, to catalyze the hydriding.

Table 2 compares film thickness times conductivity ($t \sigma$) and film thickness times Hall conductivity ($t \sigma_H$) for various candidates for use as an alternative to palladium as an overlayer.

<table>
<thead>
<tr>
<th></th>
<th>$t$ (nm)</th>
<th>$t \sigma$ ($\Omega^{-1}$)</th>
<th>$t \sigma_H$ at 0.6 T ($10^{-6} \Omega^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pd</td>
<td>20</td>
<td>0.19</td>
<td>-200</td>
</tr>
<tr>
<td>Pb</td>
<td>20</td>
<td>0.095</td>
<td>6.8</td>
</tr>
<tr>
<td>Bi</td>
<td>20</td>
<td>0.017</td>
<td>-13000</td>
</tr>
<tr>
<td>Mn</td>
<td>20</td>
<td>0.015</td>
<td>1.5</td>
</tr>
</tbody>
</table>

The alternative approach is needed if one chooses to study the rare earths.

#### 3.2. Experiment

To test Mn as an alternative overlayer, we evaporated a 200 nm layer of Dy, covered by a 16 nm layer of Mn. At first we evaporated multiple-bilayer specimens as shown in Fig. 1. However, the high film resistances (approx. 20 k$\Omega$) led to noise problems in measurement, and eventually we contented ourselves with depositing a short, single bilayer specimen.

Visual inspection of deposited films showed that the manganese overlayer succeeds in protecting the
We have developed two new techniques for removing the effect on the Hall coefficient of the Pd overlayer in bilayer hydriding studies. For studies of materials of low resistivity, the step method allows one to remove the effects of the overlayer on resistivity and Hall measurements. For materials with high resistivity, the alternative overlayer method is more effective at eliminating the Hall conduction effects of the overlayer, but at the price of very slow absorption rates. It remains unclear what causes the large variability in hydrogen absorption rates, whether the Mn decomposes molecular hydrogen or simply lets it pass, and whether there are other materials better suited than Mn to be the covering layer.

Acknowledgments

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References