

Relationship between wetting and electrical contact properties of pure metals and alloys on semiconducting barium titanate ceramics

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In this work, the relationship between the thermodynamic properties of metal–ceramic interfaces and their electrical contact properties was explored for semiconducting BaTiO₃ ceramics. The role of chemical reactivity at the interface was quantified through sessile drop measurements of the work of adhesion (W_{ad}). The interfacial properties were characterized with impedance spectroscopy to quantify contact resistance and capacitance. It was observed that interfaces with a strong chemical interaction between the metal and the oxygen anion in the ceramic showed large W_{ad} and correspondingly low contact resistances. It is believed that an oxygen depleted region near the surface of the BaTiO₃ was formed as a result of the strong metal–oxygen interactions and led to a large W_{ad} and an Ohmic contact. © 2001 Kluwer Academic Publishers

1. Introduction

The metal–ceramic interface is found in an extremely broad range of applications, such as metal–ceramic composites in structural applications, metallic electrode–electroc ceramic structures in numerous electronic applications, and metal catalysts with oxide supports in catalytic applications. The thermodynamic, electronic, and mechanical properties of interfaces can be characterized in terms of a number of fundamental physical parameters such as the thermodynamic work of adhesion (W_{ad}), Schottky barrier height Φ_B , and fracture strength. There exists considerable experimental evidence that the relative magnitudes of these parameters are strongly influenced by the crystallographic orientation relationship of the interface [1]. As all of these interfacial parameters are sensitive to the local interfacial environment, they in effect share a common fundamental relationship [2–4]. Therefore, information on the thermodynamic properties of an interface (e.g. W_{ad}) should reflect upon other parameters such as the Schottky barrier height and fracture strength, and vice versa. By using this relationship, the composition of metal–ceramic interfaces can be designed to optimize the properties for a particular application.

Brillson has illustrated the relationship between the Schottky barrier height and the chemical reactivity of the interface for a number of metals on semiconducting materials, ZnO, CdS, GaP, etc [5–7]. Interfaces in which the metal has a strong potential to react with the

substrate tend to have low barrier heights, whereas relatively inert metals tend to yield large barrier heights. Fig. 1 shows the Schottky barrier height for a number of different metals on semiconducting substrates of ZnO and ZnS as a function of the interfacial heat of reaction, written as [5]:

$$M + \frac{1}{x}CA \longrightarrow \frac{1}{x}M_xA + \frac{1}{x}C \quad (1)$$

$$\Delta H_R = \frac{1}{x}\Delta H_R^{M_xA} - \frac{1}{x}\Delta H_R^{CA} \quad (2)$$

Brillson's data clearly shows that electrodes with a strong oxygen affinity (i.e. Zn, Ti, Al) favor Ohmic contacts to semiconducting ZnO, while the noble metal interfaces exhibit large barrier heights. This same trend is seen universally for all semiconductors, although it fits best to highly ionic semiconductors which approach the Schottky limit [8].

Using data taken from a number of references [9–14], the same trend is seen for the perovskite oxides BaTiO₃, SrTiO₃, and KTaO₃ (Fig. 2). The data shows poor agreement with the Mott-Schottky equation, but the thermochemical trend is well defined [15].

The chemical interactions at a metal–ceramic interface can also be quantified in terms of the thermodynamic work of adhesion (W_{ad}). The W_{ad} is especially useful because it can be experimentally measured by a number of techniques. In the sessile drop method, the

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W_{ad} of an interface is a function of the contact angle according to the Young-Dupre equation:

$$W_{ad} = \gamma_{lv}(1 + \cos \theta) \quad (3)$$

where θ is the contact angle, and γ_{lv} is the liquid surface energy [2, 16].

A number of phenomenological models in the literature highlight the factors which determine the magni-

tude of W_{ad} for a given metal (me) and ceramic (MeO) system. The model by Chatain [3] describes the W_{ad} in terms of me-O and me-Me interactions at the interface expressed as partial enthalpies of mixing at infinite dilution, $\overline{\Delta H}_{O(me)}^\infty$ and $\overline{\Delta H}_{Me(me)}^\infty$:

$$W_{ad} = -\frac{\alpha}{\Omega} \left(\overline{\Delta H}_{O(me)}^\infty + \frac{1}{n} \overline{\Delta H}_{Me(me)}^\infty \right) \quad (4)$$

The other terms in the empirical equation are Ω the interfacial molar area, n the ratio of anions to cations in the ceramic, and α a material constant (~ 0.2 for most ceramics) [17, 18]. This equation illustrates the dependence of the wetting behavior on the strength of chemical interactions at the interface. Interfaces with strong interactions will tend to have large W_{ad} , while interfaces which interact weakly will have low W_{ad} .

By drawing together the trends seen in both the empirical model of wetting and the role of chemical reactivity in Schottky contacts, it follows that interfaces which display a large W_{ad} will tend to have low Schottky barrier heights. Furthermore, this paper aims to establish a methodology for designing the composition of alloy electrodes in terms of W_{ad} . This may allow the contact properties to be tailored in a predictable manner.

2. Experimental

The metals used in this study were all in the form of thin foils (~ 0.1 mm thick) with a purity of at least 99.99%. Metal alloys were fabricated *in situ* by measuring the appropriate quantity of each metal and melting under high vacuum conditions. Metal samples for the wetting experiments typically had masses of approximately 100 mg.

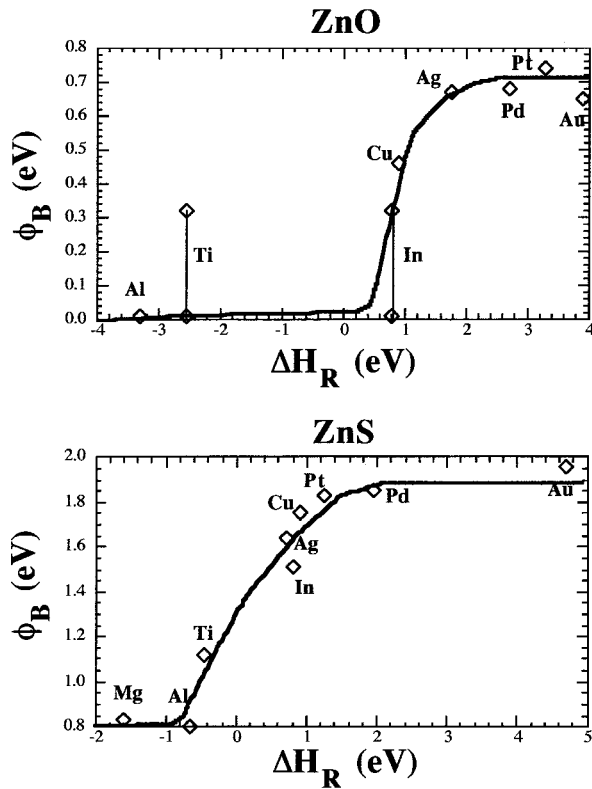


Figure 1 Schottky barrier height versus interface heat of reaction for ZnO and ZnS (adapted from Brillson [5]).

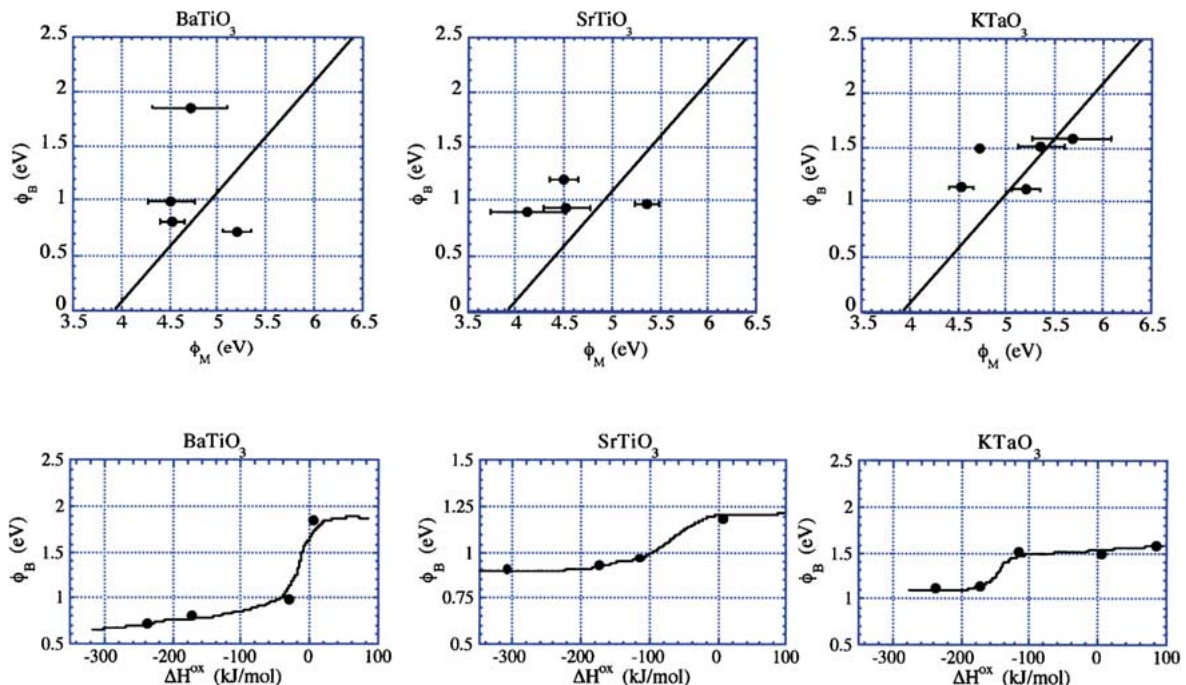


Figure 2 For highly ionic perovskite compounds BaTiO₃, SrTiO₃, and KTaO₃, a comparison of (a) Mott-Schottky rule and (b) Schottky barrier height versus heat of oxidation (ΔH_{ox}). Data taken from Refs. 9–14.

Commercial PTCR BaTiO₃ ceramic discs with a diameter of approximately 12 mm and thickness of approximately 2 mm were used in this study. The semiconducting BaTiO₃ had a resistivity in the range of 10–100 Ω-cm [19].

Sessile drop wetting experiments were conducted in a high temperature and high vacuum environment. The instrument consisted of a hinged tube furnace with SiC elements connected to standard stainless steel and aluminum vacuum components by way of a glass to metal seal at both ends of the tube. Pressures as low as 10⁻⁶ Torr were achieved with a Balzers TSH-065D Turbo-molecular Drag Pump Station which included a dry diaphragm backing pump. As compared to diffusional pumping systems, the turbo pump in combination with the dry diaphragm pump provided an oil-free environment. Pressures were measured with a cold cathode ionization gauge.

Photographs of the droplet were taken through a quartz viewport with a 35 mm camera fitted with a zoom lens and an extension tube. Contact angles were measured from enlargements of the droplet images. At the experimental temperatures in this study ($T > 900^{\circ}\text{C}$), radiation from the samples was sufficient to produce bright clear images. Due to the high rate of volatilization of liquid silver under vacuum, contact angle measurements were taken soon after melting. Therefore for the silver-based alloys in this work, the composition of the alloys at the moment the contact angles were measured were silver depleted. The thermodynamic W_{ad} was then calculated from the Young-Dupré equation.

Prior to the wetting experiments samples were cleaned by ultrasonication in acetone. Samples were placed on a graphite setter within the furnace to minimize the partial pressure of oxygen in the vicinity of the sample. Zirconia setters were also used in some wetting experiments to create a higher local partial pressure of oxygen in the vicinity of the sample. The oxygen activity could be monitored by using the known variation of the contact angle versus oxygen activity for AgAl₂O₃ obtained by Chatain [20].

Electrical measurements were made using a HP 4194A Impedance Analyzer. The solidified drops from the wetting experiments were used as one electrode and an In-Ga alloy was applied to the opposite side as the other electrode. The In-Ga alloy was found to form an Ohmic contact on PTCR BaTiO₃ in previous work [21]. Measurement frequencies ranged from 100 Hz to 10 MHz; the experiments were conducted at room temperature. The oscillating voltage utilized was typically 10 mV.

Thin film alloy electrodes were fabricated at room temperature by pulsed laser deposition (PLD) using an KrF excimer laser pulsed at 25 Hz with an energy of 350 mJ per pulse at a wavelength of 248 nm. The deposition pressures were approximately 10⁻⁵ Torr which matched the conditions at which the wetting experiments were conducted. Film thicknesses were typically on the order of 100 nm. Alloy films were constructed by rotating a target composed of the constituent foils arranged in a radial array.

Electron microprobe experiments were conducted on a Cameca SX-50 with a spot size of approximately 1 μm.

3. Results

3.1. Thermochemical properties

The wetting behavior of the metals Ag, Au, and Cu on various titanate ceramics is presented in Fig. 3. The metals were chosen because of their wide applicability in electroceramic devices. The titanates TiO₂, BaTiO₃, Ba₂Ti₉O₂₀, and (Zr, Sn)TiO₄ were chosen because of their technological importance [22]. It was observed that the W_{ad} for each of the substrates is proportional to the heat of oxidation of the metal.

$$W_{ad} = \alpha \Delta H^{ox} \quad (5)$$

This suggests that the primary interaction at the interface was between the metal and the oxygen within the substrate. This agrees with previous results on various oxides conducted by a variety of researchers, including the early model proposed by MacDonald and Eberhart [23].

One of the most thoroughly researched metal-ceramic interfaces is me-Al₂O₃. In Fig. 4, the variation in W_{ad} as a function of the heat of oxidation of the metal is shown. While there is no apparent universal trend,

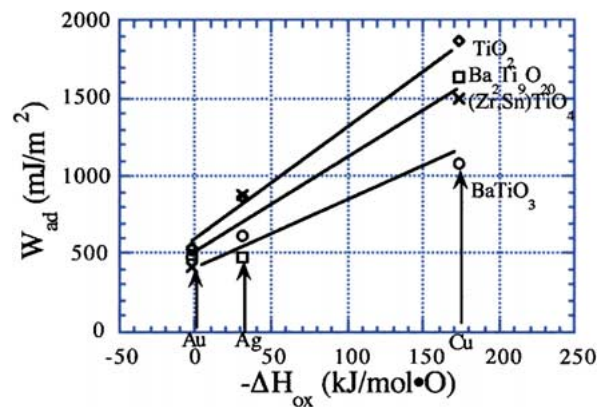


Figure 3 Experimental W_{ad} versus heat of oxidation, ΔH_{ox} for a variety of important electroceramic titanates and metal interfaces.

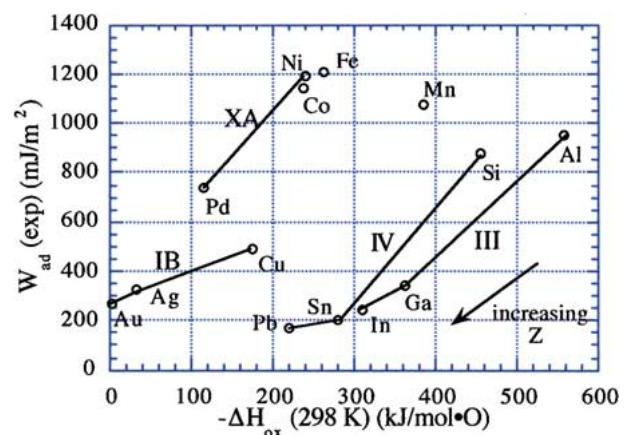


Figure 4 Graph of the heat of oxidation versus experimentally measured W_{ad} for a number of metals on Al₂O₃. Data taken from Refs 2, 3, and 4.

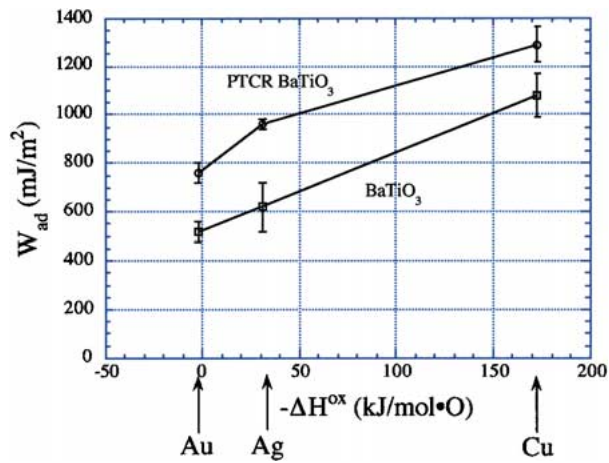


Figure 5 Comparison of work of adhesion for pure BaTiO₃ and semiconducting PTCR BaTiO₃.

within a single periodic group, the linear relationship Equation 5 holds true with reasonable accuracy. Hence for Ag, Au, and Cu, all of which are group IB metals, Equation 5 is valid. More complex models address the variation in W_{ad} for metals with different electronic structures using parameters such as the interfacial molar area Ω , and terms to include Van der Waals forces at the interface [3].

A comparison of the wetting behavior of the Ag, Au, and Cu metals on insulating and semiconducting BaTiO₃ is shown in Fig. 5. The same trend found in the other oxides was observed for PTCR BaTiO₃. It was also observed that the enhanced conductivity of the PTCR BaTiO₃ increased the W_{ad} by a constant amount of approximately 300 mJ/m². It has been proposed that the increased wettability is the result of the introduction of metallic-like bonding at the interface between the metal and conduction electrons within the semiconductor [2, 24]. It is not clear how this is affected by the fact that semiconducting BaTiO₃ is best described by the polaron conduction mechanism [25].

While metallic-like bonding is present at the interface, the results of these experiments suggest that the dominant interaction at the interface which influences the magnitude of W_{ad} on BaTiO₃ is the ionic-like bond between the electrode metal and the oxygen anion in the substrate. The magnitude of this interaction can be quantified by the heat of oxidation per mole of oxygen (ΔH_{ox} kJ · mol⁻¹ · O⁻¹). A list of the heats of oxidation for the metals in this study are listed in Table I.

Based on the ΔH_{ox} values listed in Table I, the metals Ag, Au, and Cu interact weakly with oxygen which explains the poor wetting properties of the metals. It has been shown that the addition of a secondary element

TABLE I Thermodynamic data of metals in this study

| Metal | T_m (°C) | ΔH^{ox} (kJ/mol · O) | γ_{lv} (mJ/m ²) |
|-------|------------|---------------------------------|---------------------------------------|
| Ag | 963 | -31.1 | 960 |
| Au | 1064 | +1.1 | 1185 |
| Cu | 1083 | -161.9 | 1360 |
| Ti | 1660 | -472.0 | 1410 |
| Zr | 1852 | -550.4 | 1430 |

TABLE II Wetting data for alloys on PTCR BaTiO₃. The local oxygen partial pressure was influenced by the setter: a graphite setter for low pO₂, and a zirconia for relatively high pO₂

| Alloy | pO ₂ | Θ (°) | W_{ad} (mJ/m ²) ^a |
|-----------|-----------------|--------------|---|
| Au | Low | 114 ± 2 | 700 ± 40 |
| Au-10.6Ti | Low | 79 ± 2 | 1410 ± 40 |
| Au-19.6Ti | Low | 62 ± 4 | 1740 ± 70 |
| Au | Low | 114 ± 2 | 700 ± 40 |
| Au-5.9Zr | Low | 75 ± 3 | 1490 ± 60 |
| Ag | High | 90 ± 2 | 960 ± 30 |
| Ag-2.4Ti | High | 95 ± 2 | 880 ± 30 |
| Ag-5.0Ti | High | 69 ± 11 | 1300 ± 170 |
| Ag | Low | 90 ± 2 | 960 ± 30 |
| Ag-5.7Ti | Low | 114 ± 2 | 570 ± 30 |
| Ag-6.1Ti | Low | 108 ± 9 | 670 ± 140 |
| Ag-11.6Ti | Low | 73 ± 16 | 1230 ± 250 |
| Ag | High | 91 ± 2 | 940 ± 30 |
| Ag-1.2Zr | High | 91 ± 1 | 940 ± 20 |
| Ag-2.9Zr | High | 57 ± 2 | 1480 ± 30 |
| Ag | Low | 90 ± 2 | 960 ± 30 |
| Ag-1.5Zr | Low | 115 ± 2 | 560 ± 30 |
| Ag-2.2Zr | Low | 108 ± 5 | 660 ± 80 |
| Ag-4.5Zr | Low | 100 ± 8 | 800 ± 130 |

^a W_{ad} was calculated using the surface energy of the pure solvent metal.

which has a strong affinity for oxygen can result in a significant increase in W_{ad} . This has been observed in alloys such as Cu-Ti, Ga-Ti, and Cu-Al, where Ti and Al act as the reactive solute metal [2, 24, 26–28].

Alloys were synthesized *in situ* using Ag and Au as the solvent metal, and Ti and Zr as the solute. As shown in Fig. 6 the wetting behavior of the Ti and Zr-containing alloys show a strong compositional dependence. The addition of a few molar percent solute resulted in a marked change in contact angle. The W_{ad} for the alloys was calculated using a value for the surface energy, γ_{lv} , of the pure metal. Given the high surface energy of the solute elements in this study, no significant surface enrichment would be expected [30]. Table II shows the variation in W_{ad} for the Au-Ti, Au-Zr, Ag-Ti, and Ag-Zr alloys.

Chatain *et al.* have observed that the wetting properties of liquid Ag are strongly sensitive to the experimental oxygen partial pressure [20]. In this work, the local partial pressure of oxygen could be changed by selecting a suitable substrate; either zirconia or graphite. The oxygen sensitivity of the Ag/Al₂O₃ interface is well known and can be used as a calibration of the partial pressure of oxygen in the vicinity of the liquid/solid interface. Table III lists the results of the wetting experiments of Ag on Al₂O₃ for the two different setters. The result for the zirconia setter indicate a higher local pO₂, which is a result of the reduction of ZrO₂ under these conditions. Evidence of reduction was seen by a change in color after the wetting experiments. This created a

TABLE III Contact angle of Ag on Al₂O₃ and corresponding activity of oxygen according to Chatain [20]

| Setter | Θ (°) | log a _O |
|------------------|--------------|--------------------|
| Graphite | 116 ± 4 | -3 to -5 |
| ZrO ₂ | 102 ± 4 | -1 |

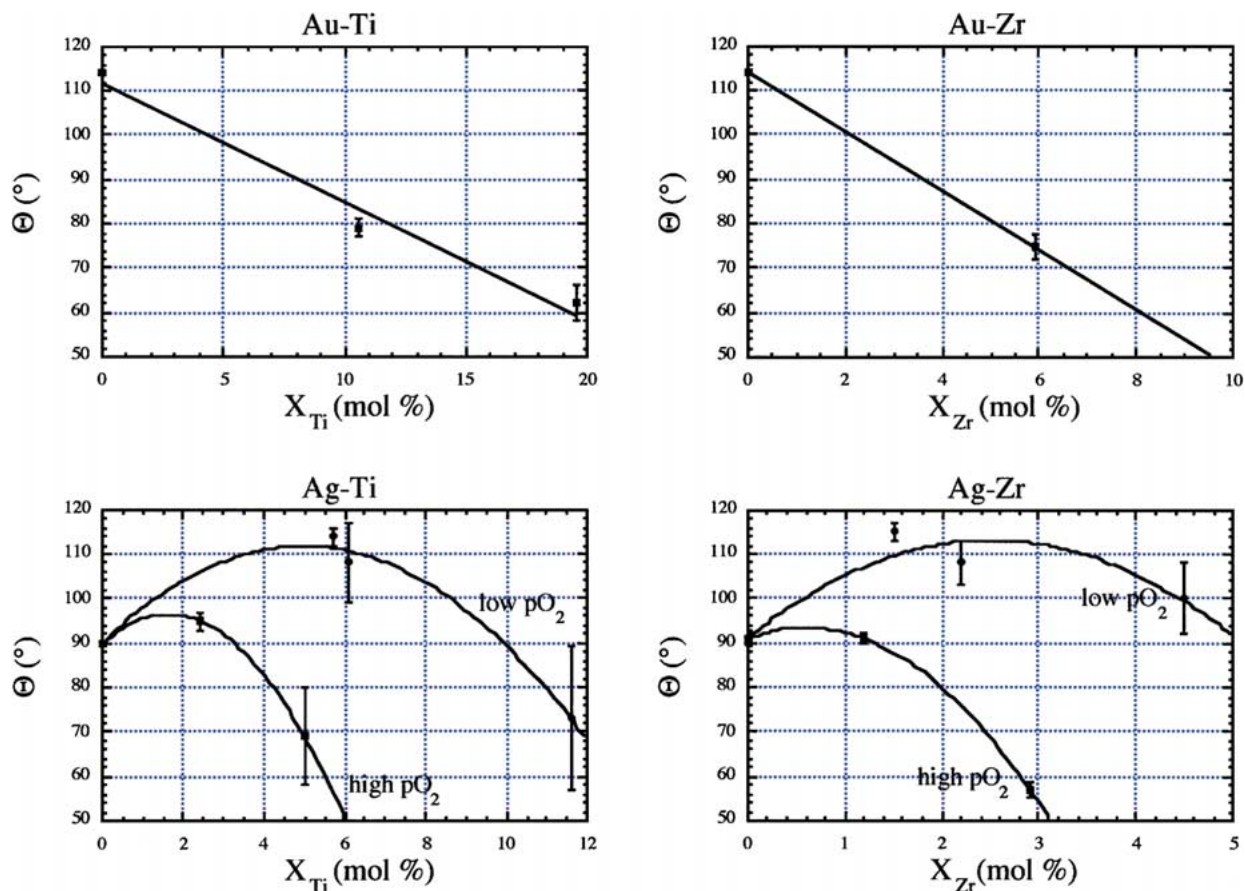


Figure 6 Comparison of wetting behavior illustrating the contact angle for Au-Ti, Au-Zr, Ag-Ti, and Ag-Zr alloys. Silver containing alloys were measured at both high and low pO_2 . All measurements were made on PTCR BaTiO₃ substrates.

source of O₂ in the vicinity of the sample which resulted in the measurement of lower contact angles.

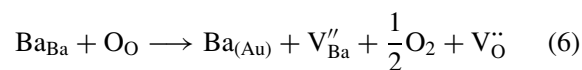
A comparison of the contact angles for the Ag-alloys for the two different setters illustrates a strong dependence on pO_2 . For a given molar percent of the Ti or Zr solute, much lower contact angles were recorded under high pO_2 conditions. Another interesting feature seen in the data was an initial increase in the contact angle for small concentrations of solute. Beyond a critical concentration the contact angle decreased significantly. The origin of this phenomena is not known, however it may be related to the segregation of the solute which is necessary to achieve low contact angles. A similar result was obtained by Wang in the Al-Cu system [26].

Kritsalis [24], Espié [31], and others [26–28] have confirmed the existence of a Ti-containing interfacial phases in alloys such as Cu-Ti which have displayed contact angles approaching 60°. It is believed that the segregation of Ti to the interface and the formation of a highly conducting phase such as TiO greatly enhances the wettability due to the introduction of metallic-like bonding. Electron microprobe experiments of the Au-Ti/BaTiO₃ interface in this work revealed the existence of a TiO_x-phase at the metal-ceramic interface. While the Au-Ti phase diagram predicts the formation of an intermetallic TiAu₄ phase for Ti concentrations greater than approximately 3 weight percent [32], the presence of oxygen in this phase suggests that it originated from an interaction with the BaTiO₃ substrate. This is consistent with the results obtained by previous workers on other metal-ceramic systems [2, 28, 31] such as

Cu-Ti/Al₂O₃. The presence of Ba was also identified with the microprobe within the metal region close to the interface.

While electron microprobe experiments were only conducted on the Au-Ti samples, cross sections of all of the samples showed a strong discoloration within the ceramic in the vicinity of the electrode visible to the naked eye. This suggests that significant reduction of the BaTiO₃ occurred. It is likely that the strong oxidative properties of Ti at the interface drew oxygen from the surface region of the BaTiO₃, resulting in a reduced layer.

The presence of Ba seen in the electron microprobe experiments could have been created by outdiffusion from the oxygen-depleted surface region. The driving force behind this phenomena may be related to the compensation of the oxygen vacancies by creating Ba vacancies in the A-site sublattice within the surface region, with the following equation utilizing the Kroger-Vink convention for the defect species [33]:



The Ba dissolved within the Au electrode is extremely stable with a large negative heat of solution of -276 kJ/mol [32].

The enhancement of the wetting properties observed in the Ti and Zr-containing alloys in this work could result from a number of mechanisms. First, electron microprobe data shows that primarily Ti resides at the

interface with BaTiO₃. The W_{ad} of pure Ti on BaTiO₃ would be expected to be very large, therefore, the large W_{ad} measured for the Au–Ti alloy may be representative of a Ti–BaTiO₃ interface. Second, if a highly conductive TiO_x phase was formed at the interface such as was observed for the Cu–Ti–Al₂O₃ system, the metallic-like bonding could result in an increased wettability [2]. Lastly, it is known that oxygen dissolved within the liquid metal can enhance wetting by the formation of metal–oxygen ionocovalent clusters which adsorb to the interface and lower the interfacial energy [3]. Any of these mechanisms are possible given the results of this research.

3.2. Electrical properties

Impedance spectroscopy was conducted on the alloy electrodes synthesized in the wetting experiments. From the geometric intercepts and maxima of the impedance data plotted in the complex plane an equivalent circuit can be ascribed to represent the experimental data. Thus, this technique can be used to separate bulk and interfacial effects in terms of a quantitative equivalent circuit [21, 34].

The impedance spectra for Au–Ti are shown in Figs 7 and 8. The data for the pure Au and Ag electrodes yields a double semi-circular configuration which is representative of a non-Ohmic contact as pictured in the equivalent circuit shown in Fig. 9. The addition of Ti resulted in a dramatic change in the impedance spectra in which the second semicircle that would indicate an interfacial barrier is non-existent, i.e. an Ohmic contact. Not shown are the results for the Zr-containing electrodes which followed a trend identical to the Ti data. Interestingly, Ti and Zr solute concentrations as low as 2–3 weight percent were able to induce the change in contact behavior. These results were confirmed in current-voltage measurements by measuring the slope (see for example Ref. 21).

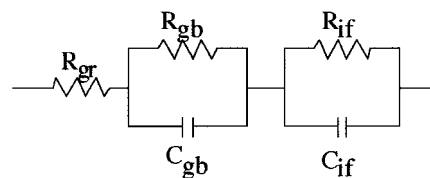


Figure 9 Equivalent circuit for PTCR ceramic, R_{gr} grain resistance, R_{gb} , C_{gb} the grain boundary resistance and capacitance, respectively, and R_{if} , C_{if} the electrode interfacial resistance and capacitance, respectively.

3.3. Thin film alloy electrodes

Thin film electrodes were fabricated with a composition based on the results obtained from the wetting experiments, Au with approximately 5 weight percent Ti. Electrode structures were deposited in four different schemes: pure Au, pure Ti, a Au/Ti bilayer electrode, and Au and Ti codeposited alloy.

The impedance spectra for the PLD electrodes are given in Fig. 10. As seen in the impedance data from the wetting experiments, Au electrodes showed a non-Ohmic contact. Pure Ti electrodes showed an Ohmic contact to the ceramic with an added series resistance ($R_{ox} \sim 20 \Omega$) indicative of an oxide scale on the surface of the Ti. The Au/Ti bilayer electrode and the (Au,Ti) codeposited electrode both showed Ohmic contacts as evidenced from the singular semi-circle in the data.

4. Discussion and summary

The wetting experiments in this study gives strong evidence that the dominant interaction at the metal–BaTiO₃ interface was between the metal and the oxygen anion in the ceramic. The W_{ad} measured in the wetting experiments was found to be dependent upon the strength of that interaction, quantified through the heat of oxidation ΔH^{ox} for pure metals.

Based on this observation, the composition of the metal was modified by the addition of Ti and Zr, which acted to enhance the me–O interactions at the interface.

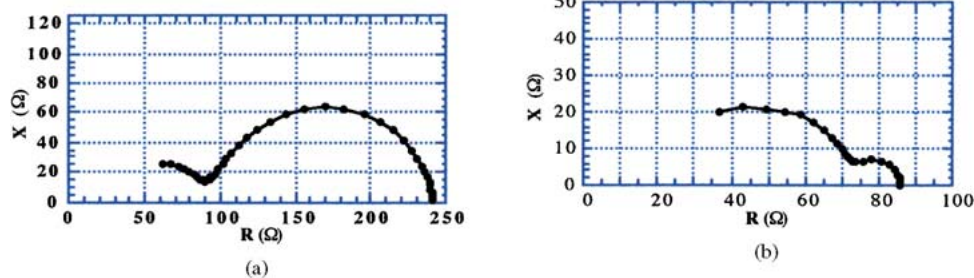


Figure 7 Impedance spectra for (a) Au–PTCR and (b) Ag–PTCR interfaces.

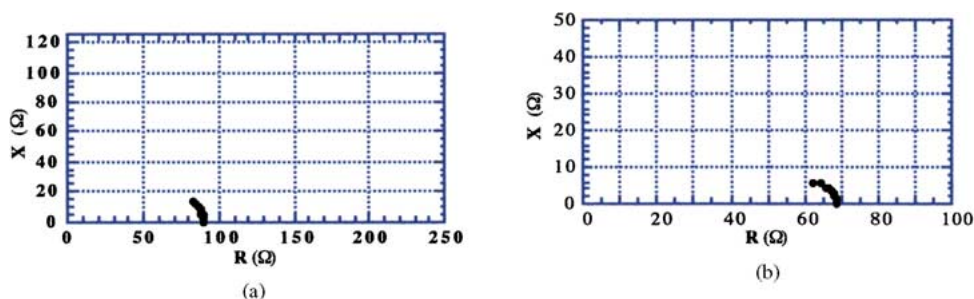


Figure 8 Impedance spectra for Ohmic contacts in (a) Au–Ti alloy, and (b) Ag–Ti alloy.

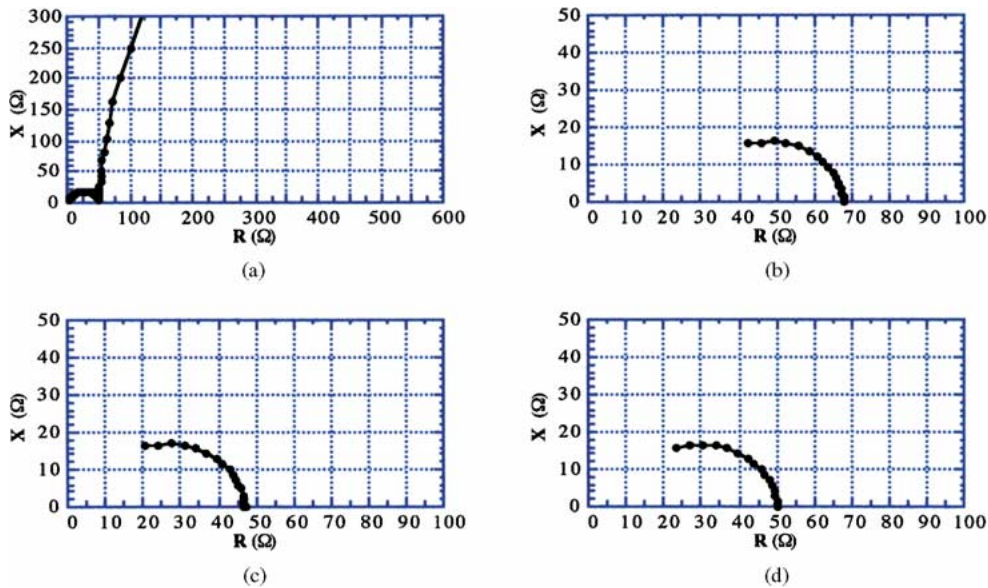


Figure 10 Impedance spectra for the thin film electrodes on PTCR BaTiO₃, (a) Au, (b) Ti, (c) Au/Ti bilayer, and (d) Au-Ti alloy.

This resulted in a large decrease in contact angle and an increase in the W_{ad} by a factor greater than two. Segregation of Ti to the electrode/BaTiO₃ interface was observed along with strong discoloration in the interface region of the ceramic. All of these observations suggest that Ti enhanced the me-O interactions at the interface and thereby drew oxygen from the surface region of the BaTiO₃, which resulted in a high density of oxygen vacancies.

The Ohmic contacts observed for the alloy electrodes also support this hypothesis. According to Brillson [6], since BaTiO₃ is a highly ionic compound the Mott-Schottky equation is valid, thus [15]:

$$\Phi_B = \Phi_M - \chi_{BaTiO_3} \quad (7)$$

Where Φ_B is the Schottky barrier height, Φ_M is the metal work function, and χ_{BaTiO_3} is the electron affinity. For interfaces in which Φ_M is less than χ_{BaTiO_3} , an ideal Ohmic contact such as pictured in Fig. 11a is achieved. For BaTiO₃, the electron affinity has been estimated to be 3.9 eV [14]. Thus, metals with $\Phi_M < 3.9$ eV should yield Ohmic contacts. However, as shown in Table IV, the Φ_M values for the metals in this study were all greater than 3.9 eV, which excludes the interface structure pictured in Fig. 11a [35].

Instead, the Ohmic properties measured in impedance and current-voltage measurements resulted from the creation of a heavily doped surface layer in the BaTiO₃ (Fig. 11b). The width of a Schottky barrier decreases with heavy doping according to the equation [15]:

$$W_{sc} \propto N_D^{-\frac{1}{2}} \quad (8)$$

TABLE IV Work functions for the metals in this work [35]

| Metal | Φ_M (eV) |
|-------|---------------|
| Zr | 4.05 |
| Ti | 4.33 |
| Ag | 4.26-4.74 |
| Au | 4.3-5.1 |

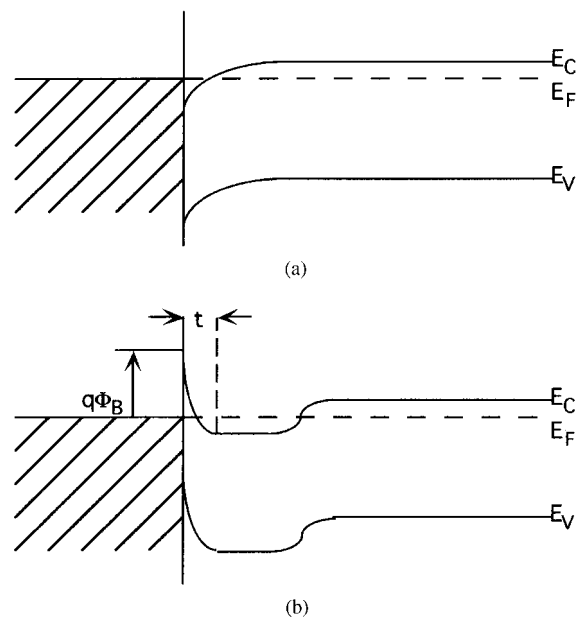


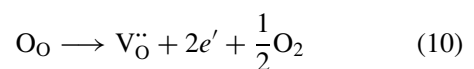
Figure 11 Two possible Ohmic contact structures (a) $\phi_M < \chi_{S/C}$, and (b) tunneling contact for heavily doped surface layer.

where W_{sc} is the width of the space charge layer and N_D is the donor density. As the barrier width shrinks, tunneling across the barrier becomes possible and the overall resistance of the contact decreases as:

$$R_c \propto \exp\left(\Phi_B \cdot N_D^{-\frac{1}{2}}\right) \quad (9)$$

Where R_C is the contact resistance [15].

Thus, the electrical data could support that fact that the heavily donor doped region was created by the extraction of oxygen from the surface region of the ceramic, creating oxygen vacancies which act as donor sites, viz.:



The oxygen was drawn from the surface by the addition of the highly oxidative Ti and Zr elements. The Ohmic contacts achieved with PLD alloy electrodes suggest

that the oxidizing properties of Ti are sufficiently strong to reduce the surface layer of BaTiO₃ even at room temperature.

Recalling Fig. 1, it has been shown that the same relationship between interfacial reactivity and electrical contact properties exists for semiconducting BaTiO₃ ceramics. In this work the chemical reactivity was directly measured in terms of the thermodynamic W_{ad} .

5. Conclusions

In this work, the fundamental relationship between thermochemical interactions at a metal–ceramic interface and the electrical contact properties was explored for semiconducting BaTiO₃. From wetting experiments, the dominant interaction which determined the magnitude of W_{ad} was observed to be the metal–oxygen interaction. Alloy electrode compositions designed to enhance this interaction showed improved wetting properties.

The addition of Ti and Zr in the form of an alloy transformed the contact structure from non-Ohmic to Ohmic. The strong me–O interactions induced by the addition of Ti resulted in the formation of a oxygen depleted layer within the ceramic. The oxygen vacancies in this region formed a heavily doped layer which acted to decrease the Schottky barrier width to allow tunneling.

Thus, the interrelationship between the thermochemical properties of an interface and its electrical contact properties can be used to apply a scientific methodology to design the composition of electrode metals in order to obtain optimum properties.

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