**Supplementary Information for:**

# Chemical State Determination of Molecular Gallium Compounds using XPS

Jeremy L. Bourque,[1] Mark C. Biesinger[2] and Kim M. Baines*[1]

[1] Department of Chemistry, University of Western Ontario, London, Ontario, Canada N6A 5B7

[2] Surface Science Western, University of Western Ontario, London, Ontario, Canada, N6G 0J3

**Table S1: Tabulated survey scans for compounds 1 - 15, 19.**

| Compound | Atomic Percentage (%) | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | **C** | **N** | **O** | **F** | **Na** | **Mg** | **Si** | **S** | **Cl** | **K** | **Ca** | **Ga** | **Br** | **I** |
| **1** | 56.5 | - | 19.1 | 0.3 | - | - | - | - | 14.3 | - | - | 9.5 | - | 0.4 |
| **2** | 50.3 | - | 21.7 | 7.2 | - | - | - | - | 12.1 | - | - | 8.6 | - | - |
| **3** | 57.1 | - | 23.9 | 9.6 | - | - | - | 2.6 | - | - | - | 2.3 | - | 4.5 |
| **4** | 90.3 | 3.5 | 2.2 | - | - | - | - | - | 0.3 | - | - | 3.1 | - | 0.6 |
| **5** | 65.5 | - | 18.1 | 1.3 | - | - | 0.3 | - | 2.7 | 8.9 | - | 2.2 | - | 0.9 |
| **6** | 50.3 | - | 25.0 | 15.8 | - | - | 1.8 | 5.0 | - | - | - | 2.0 | - | 0.1 |
| **7** | 51.7 | - | 19.0 | - | - | - | - | - | 19.9 | - | - | 9.5 | - | - |
| **8** | 68.7 | - | 15.1 | - | - | - | - | - | - | - | - | 6.5 | - | 9.7 |
| **9** | 85.1 | - | 8.3 | - | - | - | - | - | - | - | - | 3.5 | - | 3.1 |
| **10** | 41.9 | - | 17.0 | 5.6 | 0.4 | - | - | - | 21.8 | - | - | 13.4 | - | - |
| **11** | 67.5 | - | 10.0 | 1.4 | 0.2 | - | - | - | - | - | - | 6.9 | 12.6 | 1.3 |
| **12** | 53.4 | - | 10.2 | - | - | - | - | - | - | - | - | 8.2 | - | 28.3 |
| **13** | 42.6 | - | 20.3 | 3.6 | - | 0.6 | - | - | 19.7 | - | 0.6 | 12.2 | - | 0.3 |
| **14** | 34.9 | - | 10.0 | 42.4 | - | - | - | - | 7.8 | - | - | 4.9 | - | - |
| **15** | 55.1 | - | 16.0 | 18.3 | - | - | - | - | - | - | - | 4.2 | - | 6.4 |
| **19** | 8.7 | - | 55.5 | - | - | - | - | - | 0.2 | - | - | 35.5 | - | - |

Note: Varying levels of contamination were observed for most of the samples analyzed. Common contaminants were found to be iodine, oxygen, carbon, and fluorine. The source of the iodine is postulated to come from cross-contamination arising from the vacuum chamber of the XPS instrument, as it was not only observed in samples related to this study, but in other data

from unrelated work. Carbon and oxygen arise from the adhesive tape used in sample preparation. Alternatively, the oxygen could have been a result of possible oxidation of the samples. Despite the use of an argon filled glovebox for sample preparation and introduction to the XPS instrument, the sensitivity of the gallium compounds to oxygen and water could have lead to some oxidation on the surface of some samples, causing oxygen contamination, however, because of the strict anaerobic conditions employed, this was assumed to be negligible. Any additional carbon and oxygen contamination could be resulting from excess solvent present in the samples, due to incomplete drying. The presence of fluorine in the survey spectra is likely a result of the fluoropolymer lining in the sample vial caps, which were used for synthesis and transportation of the samples. Overall, none of the contaminants were believed to interfere with any of the results of this study, as the gallium signals were used for characterization and assignment for all compounds, of which there was no contamination source.

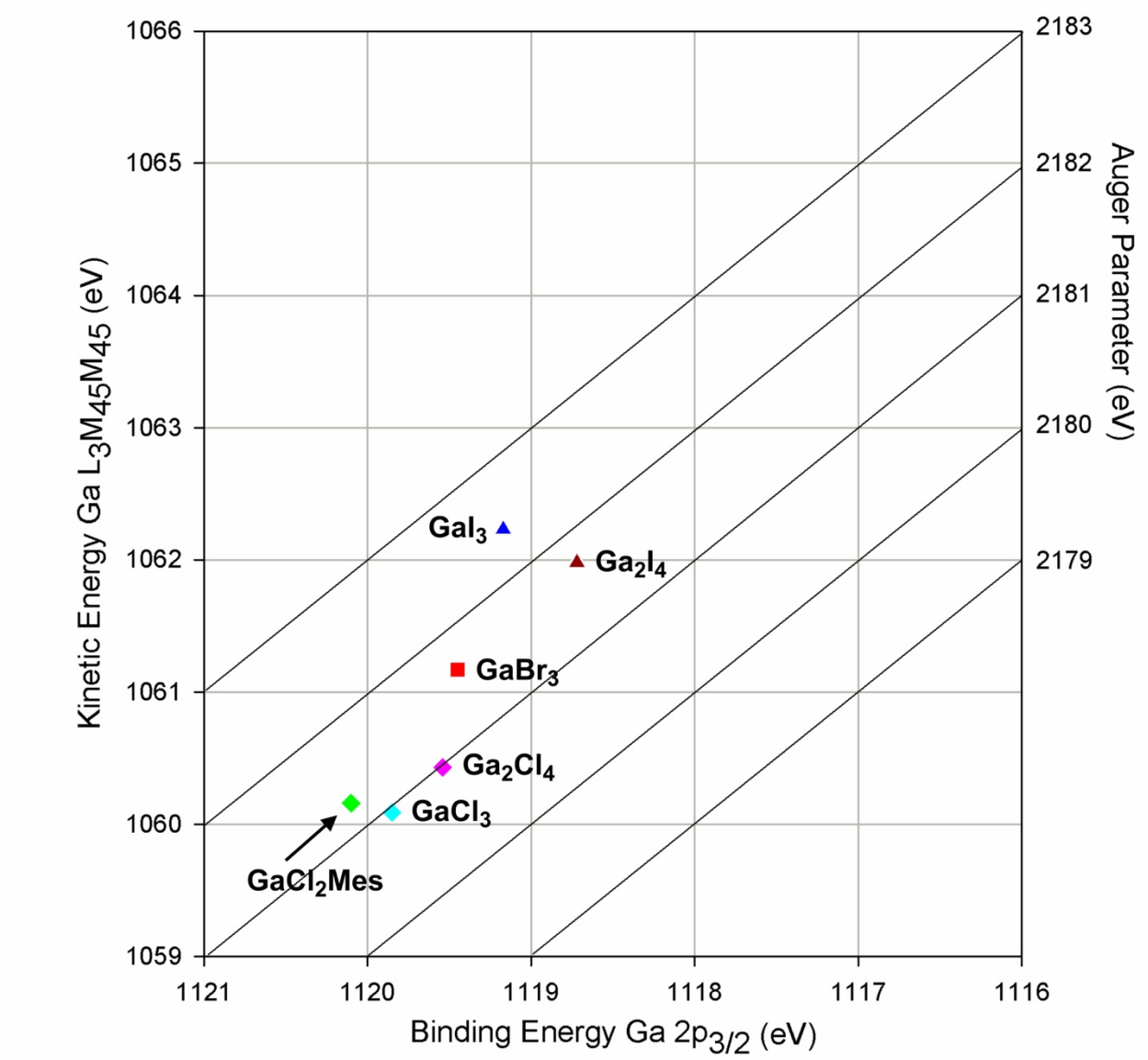


**Figure S1: Wagner plot of gallium halides using Ga $2p_{3/2}$ binding energy. Symbol legend: diamond = chloride ligands; square = bromide ligands; triangle = iodide ligands.**

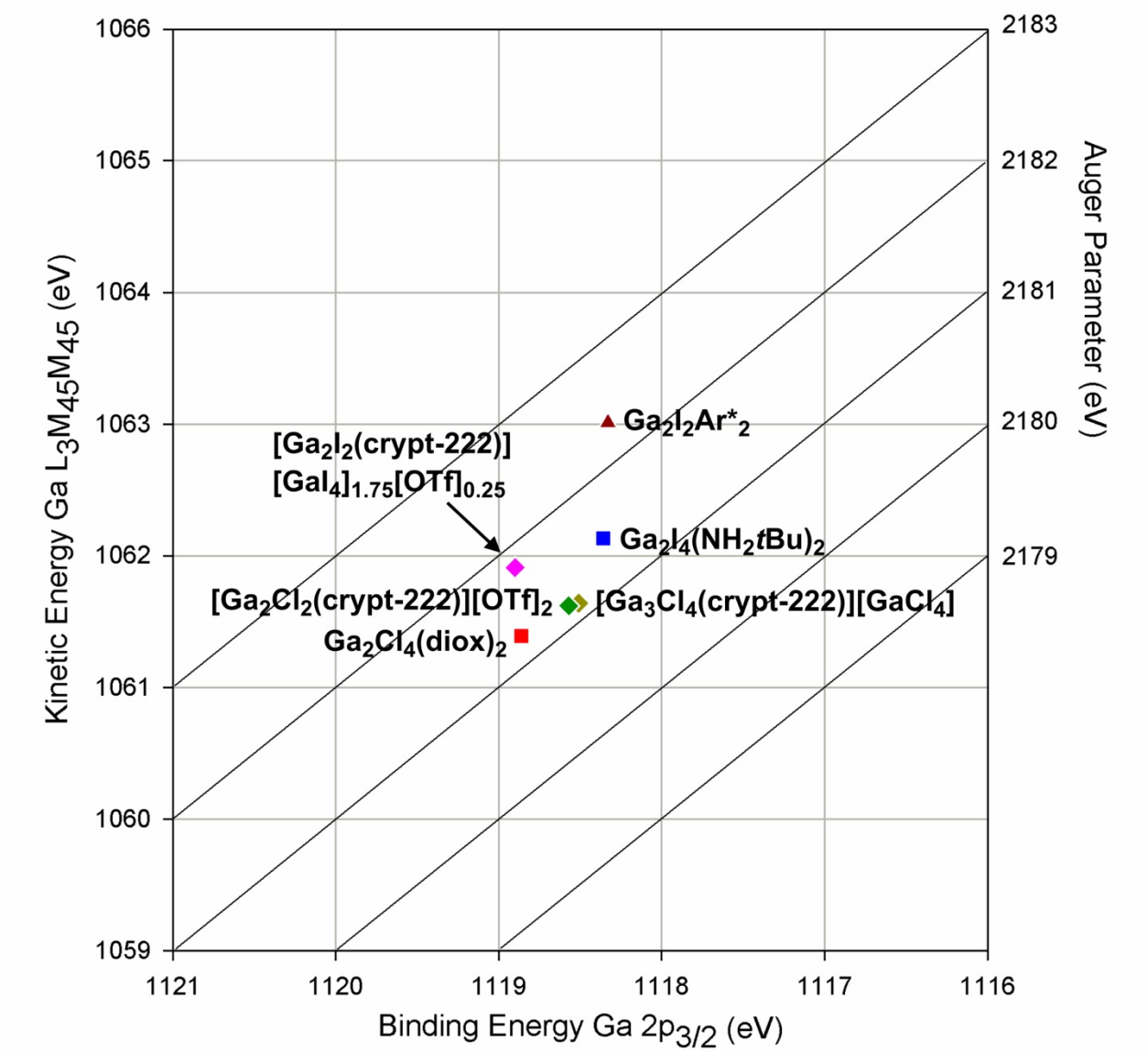


**Figure S2: Wagner plot of Ga-Ga compounds using Ga $2p_{3/2}$ binding energy. Symbol legend: diamond = synthesized gallium-cryptand complexes; square = chloride and iodide ligands and O/N donors; triangle = iodide and terphenyl ligands.**

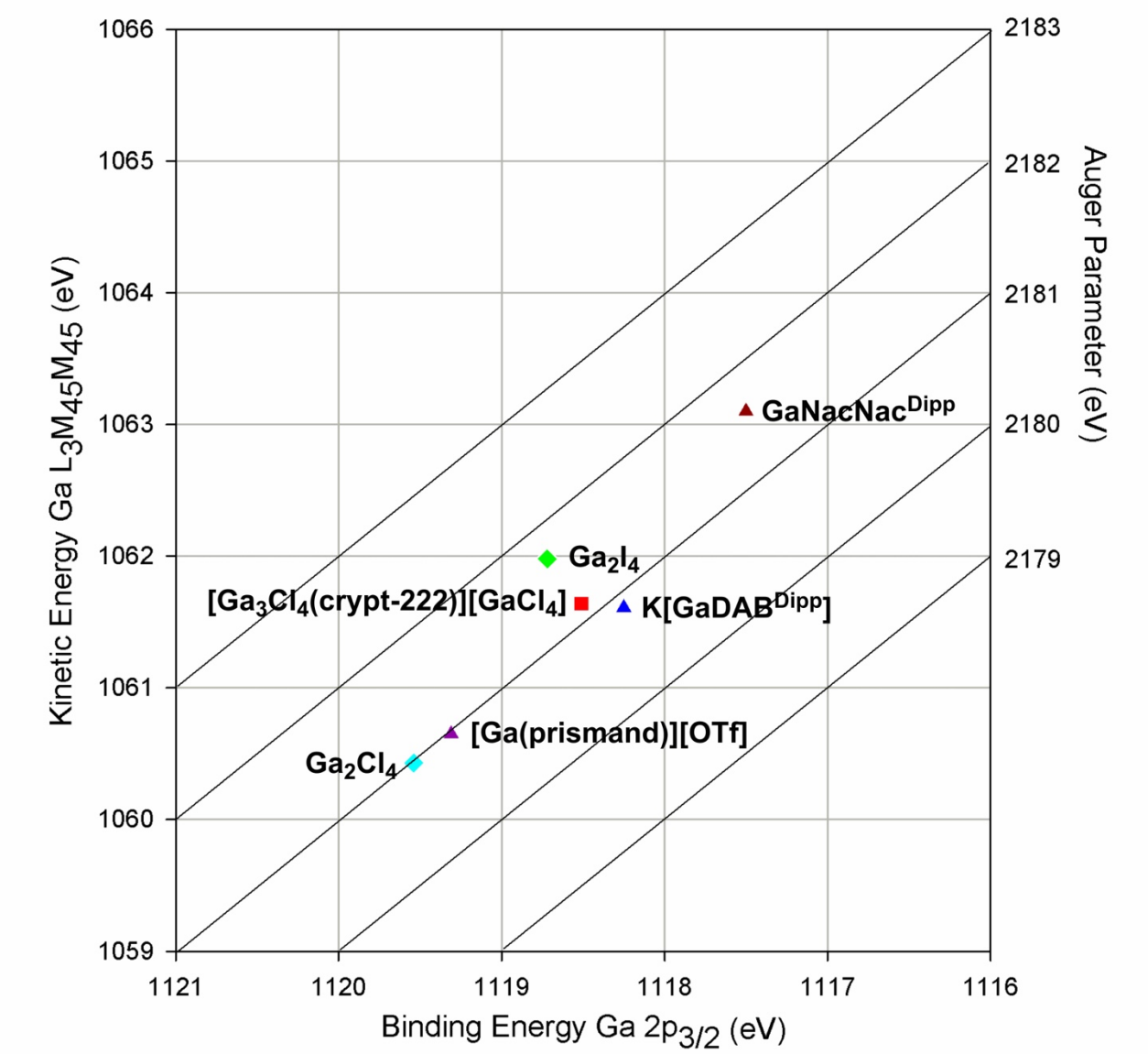


**Figure S3: Wagner plot of Ga(I) compounds using Ga $2p_{3/2}$ binding energy. Symbol legend: diamond = halide ligands; square = chloride ligands and O/N donors; triangle = organic ligands.**

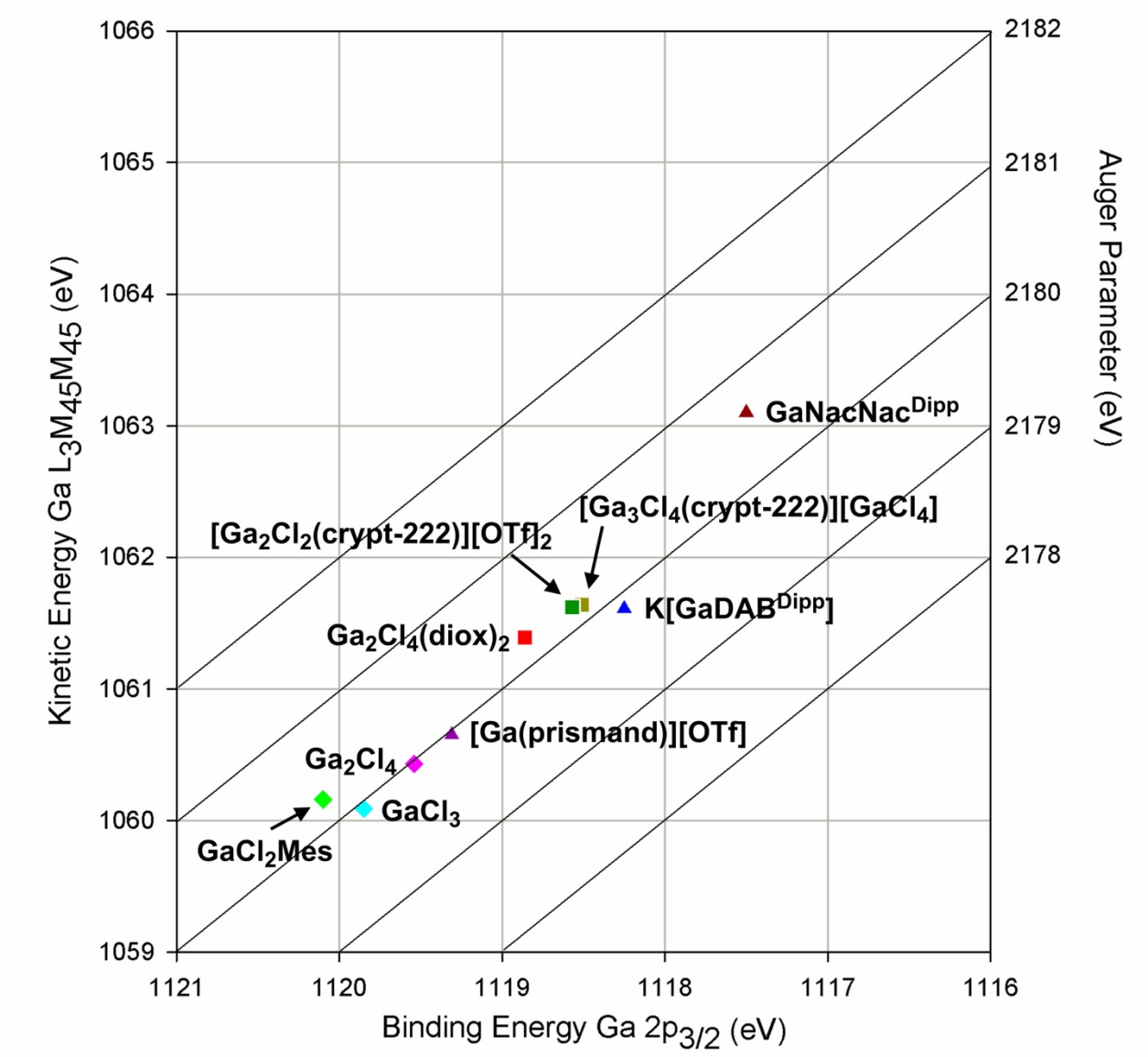


**Figure S4: Wagner plot of gallium-chloride and gallium-nitrogen compounds using Ga $2p_{3/2}$ binding energy. Symbol legend: diamond = Ga(III); square = Ga(II); triangle = Ga(I).**

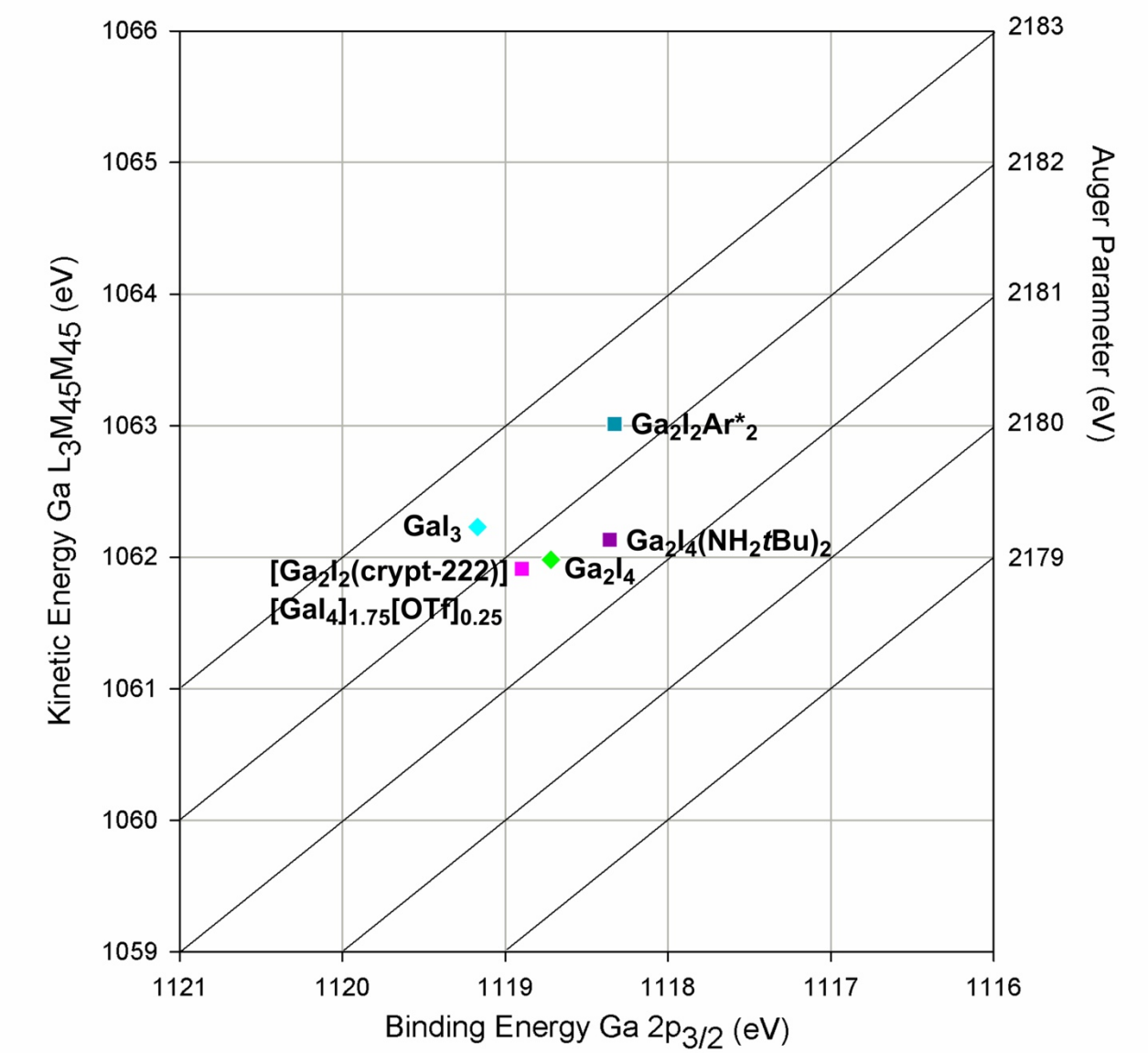


**Figure S5: Wagner plot of gallium-iodide compounds using Ga $2p_{3/2}$ binding energy. Symbol legend: diamond = Ga(III); square = Ga(II).**

**Table S2: Auger parameters and relevant shifts for compounds analyzed using Ga $2p_{3/2}$ binding energy.**

| Compound | Auger Parameter, $\alpha'$ (eV) | $\Delta E_B$ (eV) | $\Delta E_K$ (eV) | Relaxation Shift, $\Delta\alpha'$ (eV) | Final State Shift, $\Delta R$ (eV) | Initial State Shift, $\Delta\varepsilon$ (eV) |
|---|---|---|---|---|---|---|
| **$Ga_{(m)}$** (meas) | 2184.50 | - | - | - | - | - |
| **$Ga_{(m)}$** (lit) | 2184.88 | - | - | - | - | - |
| **4** | 2180.60 | 1.01 | -4.91 | -3.90 | -1.95 | 0.94 |
| **5** | 2180.86 | 1.76 | -6.40 | -4.64 | -2.32 | 0.56 |
| **6** | 2180.96 | 2.82 | -7.36 | -3.54 | -1.77 | -1.05 |
| **7** | 2180.25 | 2.37 | -6.62 | -4.25 | -2.13 | -0.25 |
| **8** | 2180.49 | 1.87 | -5.88 | -4.01 | -2.01 | 0.14 |
| **9** | 2181.34 | 1.84 | -5.00 | -3.16 | -1.58 | -0.26 |
| **10** | 2179.94 | 3.36 | -7.92 | -4.56 | -2.28 | -1.08 |
| **11** | 2180.62 | 2.96 | -6.84 | -3.88 | -1.94 | -1.02 |
| **12** | 2181.40 | 2.68 | -5.78 | -3.10 | -1.55 | -1.13 |
| **13** | 2180.26 | 3.61 | -7.85 | -4.24 | -2.12 | -1.49 |
| **14** | 2179.97 | 3.05 | -7.58 | -4.53 | -2.27 | -0.79 |
| **15** | 2180.70 | 2.23 | -6.03 | -3.80 | -1.90 | -0.33 |
| **18** | 2183.30 | 0.41 | -1.61 | -1.20 | -0.60 | 0.19 |
| **19** (meas) | 2180.40 | 1.31 | -5.41 | -4.10 | -2.05 | 0.74 |
| **19** (lit) | 2180.25 | 0.96 | -5.16 | -4.25 | -2.13 | 1.22 |
| **1** | 2180.15 | 2.02 | -6.37 | -4.35 | -2.18 | 0.16 |
| **2** | 2180.19 | 2.08 | -6.39 | -4.31 | -2.16 | 0.08 |
| **3** | 2180.81 | 2.41 | -6.10 | -3.69 | -1.85 | -0.57 |