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PII: S1359-8368(22)00579-0
DOI: https://doi.org/10.1016/j.compositesb.2022.110205
Reference: JCOMB 110205

To appear in: Composites Part B

Received Date: 18 May 2022
Revised Date: 28 July 2022
Accepted Date: 10 August 2022


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**ABSTRACT**

We study the piezoelectric behavior of metal-doped monolayer MoS$_2$. Its three-dimensional charge density, work function (WF), and piezoresponse with various metal dopants are theoretically predicted based on density functional theory, and the real-time piezoelectric power of these samples is experimentally verified. Selected $p$-type metal dopants (Au, Ag, Pd, Pt, and Al) increase the WF of monolayer MoS$_2$, affecting electron emission from the MoS$_2$ surface. The reason is that $p$-type metal dopants suppress excess electrons and prevent screening effects. A nanogenerator constructed from Au-doped monolayer MoS$_2$ has been used to explore the possibility of a practical device.

**GRAPHICAL ABSTRACT**

**KEYWORDS**

Piezoelectric, Molybdenum disulfide, Metal doping, Density functional theory
The piezoelectric effect is a phenomenon in which electric energy is generated by the accumulation of electric charges in a specific material due to deformation. Molybdenum disulfide (MoS\(_2\)), one of the two-dimensional (2D) materials with atomic layer thickness, has a high piezoelectric constant and flexibility in the plane direction, so it reacts very sensitively to deformation [1-3]. Since it is possible to generate an electric signal, it has the advantage that various applications can be explored [4-7].

Since the piezoelectric properties of a material appear when the size or direction of the polarization changes, the response depends on the direction of the polarization in its crystals, the symmetry of the crystals, the applied mechanical stress, etc [8]. In addition, the inevitable defects (e.g., vacancies) occurring in the material synthesis generate extra carriers, causing degradation of the piezoelectric phenomenon. To overcome this, the carrier density is controlled through heat treatment and defect passivation [2, 9-11]. Heat treatment, however, has the disadvantage that there is a limitation in the process when using a flexible substrate, etc., and excessive sulfur occurs during the sulfur control process through passivation.

Chemical doping is an easy method used to change the electrical properties by affecting the band structure of a semiconductor material [12-15]. The possible doping materials are known to be metallic gold (Au) [16-18], phosphorus (P) [19-23], niobium (Nb) [24-26], manganese (Mn) [27-30], zinc (Zn) [31-33], and iron (Fe) [34-35], as well as organic compounds such as magic blue (tris(4-bromophenyl)ammoniumyl hexachloroantimonate) [36-39], 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F4TCNQ) [40-42], and 7,7,8,8-tetracyanoquinodimethane (TCNQ) [42, 43-44]. An effective means of piezoelectric enhancement is preventing the screening effect by removing extra carriers. Since MoS\(_2\) has \textit{n}-type semiconductor characteristics, it is usual to reduce excess electrons through \textit{p}-doping to
suppress screening effects and improve piezoelectric characteristics. There are various metals used for $p$-type doping of MoS$_2$ [16-18, 24-35]. Among these, MoS$_2$ doped with Au has aroused tremendous interest because Au has the highest magnetic moment compared to other dopants, and the first half of the $d$-band is completely coupled to create a stable fully polarized state. It is important to understand how the dopant affects the electric structure, but to the best of our knowledge, the correlation between the electronic structure and the piezoelectric properties of MoS$_2$ after doping remains controversial.

In this study, we have verified why Au is an effective chemical doping element for monolayer MoS2 and how the dopant affects the electronic structure and piezoelectric behavior based on density functional theory (DFT). Strong charge redistribution is observed due to the interaction between Au and MoS$_2$, and how the work function (WF) changes according to strain effects is described computationally. It is also shown that the piezoelectric property of Au-doped MoS$_2$ is improved compared to pristine MoS$_2$ through experimental results. This study provides an understanding of the relationship of electronic structure changes in Au-doped MoS$_2$ by explaining the reason Au dopant effect to the piezoelectric properties in MoS$_2$ through the electronic structure. Furthermore, we present a theoretical knowledge for the effect of doping materials on the piezoelectric properties of MoS$_2$.

Fig. 1 shows the DFT calculation results on the change in WF when various metals are doped onto monolayer MoS$_2$. A detailed description of the computation method is included in the Supporting Information. The interaction between MoS$_2$ and the metal dopants implies a substantial charge transfer between the involved constituents. This can be visualized as shown in Fig. 1a by a three-dimensional (3D) charge density difference. The metal dopant elements considered in this study are gold (Au), silver (Ag), palladium (Pd), platinum (Pt), and aluminium (Al). When the metal is doped on the MoS$_2$ monolayer, charge accumulation occurs
on its surface, as shown in the yellow isosurface on the right of Fig. 1a.

Before calculating the charge density change to the position where the metal is doped on the MoS$_2$ needs to be considered. Charge redistribution can be observed by taking the interaction between Au, the most well-known metal dopant, and MoS$_2$ as an example. The relaxed structures in which Au can be doped into monolayer MoS$_2$ include hole sites, Mo sites, and substitution at the S position, as shown in Fig. S1. A strong charge accumulation is formed in the topmost sulfur (S) layer of the monolayer MoS$_2$, and a charge deficiency is found just above the doped Au atoms (yellow isosurface on the right of Fig. 1a). Adding an Au atom on MoS$_2$ causes a charge redistribution. The charge is accumulated near Au atoms, however, and the electron losses occur in the topmost sulfur layer on MoS$_2$, owing to the different atomic binding. Substituting Au for S was found to change the electronic structure of Mo and S. A small electron deficiency is observed in the bottom-most S layer of the MoS$_2$ (Fig. S1).

Pristine monolayer MoS$_2$ is a direct semiconductor with a band gap ($E_g$) of 1.730 eV, which agrees well with previous experiments and theoretical studies. The conduction band bottom of pure MoS$_2$ mainly consists of Mo 4d and S 3p states, while the upper valence band is composed of Mo 4d states. When Au is doped onto the monolayer, the band gap is lowered to 0.560 eV, and the Fermi level is shifted to the lower value of -3.12 eV from -2.51 eV (pristine monolayer MoS$_2$), as shown in Fig. 1b. Au contributes to the valence band due to bonding generation with Mo. The calculated change in Fermi level according to the doping with each element is shown in Fig. 1b and Fig. S2. Apart from Al, Ag, Pd, and Pt all also shifted the Fermi level to the lower values of -2.89, -2.86, and -2.71 eV from -2.51 eV, respectively. As their Fermi level is lowered, their WF increases in the range of 0.279 to 0.761 eV, as shown in Fig. S3. Fig. 1c and Table S1 shows the WF change when each element is doped by reflecting the shift in the Fermi-level based on the calculation results and previous research respectively. Au showed the largest
Fermi-level shift and WF increase, and it was closer to the intrinsic Fermi-level. This suggests that Au doping is an effective way to improve the piezoelectric property of MoS$_2$, removing the extra carriers and thus preventing the screen effect. Accordingly, Au was selected as the most desirable metal for doping of monolayer MoS$_2$, and the WF change by chemical doping of monolayer MoS$_2$ was experimentally confirmed using AuCl$_3$ solution.

Monolayer MoS$_2$ was synthesized by the chemical vapor deposition method (CVD) using MoO$_3$ powder and H$_2$S gas as precursors. The synthesis of MoS$_2$ and the Au doping method using AuCl$_3$ solution are described in detail in the Supporting Information. Fig. 2 shows the experimental results of the WF change of monolayer MoS$_2$ before and after Au doping through atomic force microscopy (AFM), Kelvin probe force microscopy (KPFM), and X-ray photoelectron spectroscopy (XPS) measurements. Fig. 2a is an AFM image showing the surface topology of pristine MoS$_2$ and Au-doped MoS$_2$. The surface roughness of pristine MoS$_2$ and Au-doped MoS$_2$ at 5 $\mu$m $\times$ 5 $\mu$m was 0.57 nm and 0.61 nm, respectively, showing a very flat surface without any noticeable difference. In the KPFM images of Fig. 2b, the WF values of pristine MoS$_2$ and Au-doped MoS$_2$ were measured to be 5.13 $\pm$ 0.2 eV and 5.46 $\pm$ 0.2 eV, respectively, showing differences. The diagram in the KPFM mapping image in Fig. 2b shows the Fermi-level changes of pristine MoS$_2$ and Au-doped MoS$_2$. After Au doping, the work function of MoS$_2$ increases by about 0.33 eV, which means that the Fermi level is close to the intrinsic Fermi level. This result is good agreement with the calculation result in Fig. 1. XPS spectra are also an experimental result demonstrating the binding energy shift of MoS$_2$. Fig. 2c and Fig. S4 show the Mo 3d and S 2p peaks of MoS$_2$ before and after the Au doping process.

First, the stoichiometric ratio of the synthesized MoS$_2$ confirmed through the XPS result was found to be Mo : S = 1: 1.87, and it can be confirmed that the Mo 3d and S 2s peaks were downshifted ($\sim$ 0.29 eV) after Au doping. Mo 3d$_{3/2}$ shifts from 232.94 to 232.65 eV, Mo 3d$_{5/2}$
shifts from 229.72 to 229.43 eV, and S 2s shifts from 226.97 to 226.68 eV. The downshift of the peaks is directly attributed to the $p$-doping, since it causes a Fermi level shift toward the valence band edge, and the Fermi level is where the zero energy lies [2]. In addition to the Mo 3d and S 2s peaks, the S 2p peak of Fig. S4 does not show results such as a peak appearing at a new position after Au doping, which means that no new chemical bonds were formed due to doping. It shows the same shift in direction and value as the Mo 3d and S 2s peaks in Fig. 2c, proving the shift of the Fermi level. The WF change caused by Au doping is clearly confirmed through calculations and experimental results.

The XPS peaks of Au 4f and Cl 2p prove that the doping MoS$_2$ by using an AuCl$_3$ solution was successful. The Au 4f peak in Fig. S5 indicates that AuCl$^-$ ions are completely reduced to Au, and Cl 2p with no peaks means that there is no physical adsorption of AuCl$_4$ ions. The topography images in Fig. S6 shows that Au particles growth on MoS$_2$ surface after doping process compared with pristine MoS$_2$. The process of doping Au through AuCl$_3$ solution is as follows: AuCl$_3$ particles react with nitromethane as a solvent to produce AuCl$_4$, and AuCl$_4$ ions are reduced to Au particles by recovered electrons from MoS$_2$ [45]. It was also determined through XPS whether the degree of doping changes when MoS$_2$ is doped using different numbers of moles of AuCl$_3$ in the doping solution. As shown in Fig. S7, when monolayer MoS$_2$ was chemically doped using 5 mM and 10 mM AuCl$_3$ solutions, respectively, the Mo 3d peak was downshifted to 229.41 eV and 229.43 eV, respectively, from 229.72 eV (pristine MoS$_2$). The downshifted range was 0.31 to 0.29 eV, meaning that there was no significant difference in the degree of doping according to the difference in moles and that the Au was doped successfully.

Based on the WF shift confirmed by Au doping, a piezoelectric nanogenerator (PENG) was fabricated to determine whether the piezoelectric properties of monolayer MoS$_2$ were improved.
Fig. 3a shows the actual image and detailed structure of the PENG on a flexible substrate. The device fabrication process is described in detail in the Supporting Information. A flexible polyethylene terephthalate (PET) substrate was used for bending, and the electrodes were deposited in the order of chromium (Cr), palladium (Pd), and gold. It was confirmed that the MoS$_2$ nanosheet used in the PENG was a monolayer through the Raman spectrum and AFM. The AFM topographical image and line profile in Fig. 3a and the Raman results in Fig. S8 indicate that the synthesized MoS$_2$ was a monolayer. The frequency difference between the out-of-plane ($A_{1g}$) and in-plane ($E^{12g}$) phonon modes was used to confirm the layer of MoS$_2$, and the difference value was 19, which means monolayer (Fig. S8). In addition, the height of 0.7 nm obtained through the AFM result indicates that the thickness of MoS$_2$ was monolayer, as shown in Fig. 3a. It can also be confirmed that there is no change in MoS$_2$ after Au doping, in light of the fact that no shift or new peak appears on the Raman spectrum after Au doping.

Piezoresponse force microscopy (PFM) analysis, which is one of the methods for detecting the piezoelectric characteristics of piezoelectric materials, was performed before testing the output power change. This is the method used to analyze the piezoelectric and reverse piezoelectric effect of materials by testing the electromechanical coupling properties. This is done by applying a set voltage to form an external electric field in the sample and measuring the degree to which the sample expands or contracts locally along the electric field. Au electrodes were deposited on the sapphire substrate edges of both pristine MoS$_2$ and Au-doped MoS$_2$ to calculate the piezoelectric coefficient $d_{11}$ in the lateral direction by applying an external electric field in the lateral direction. The PFM system used to measure the piezoelectric coefficient is shown in Fig. S9. Fig. 3b shows the piezoresponse as a function of the magnitude of the external bias applied to $\alpha$-quartz, pristine MoS$_2$, and Au doped MoS$_2$. The $\alpha$-quartz was used as a reference, and since the lateral piezoelectric coefficient $d_{11}$ of $\alpha$-quartz is known to
be about 2.3 pm/V, it can be used to correct the piezoelectric coefficient of MoS\textsubscript{2}. Compared to \(\alpha\)-quartz, both pristine MoS\textsubscript{2} and Au-doped MoS\textsubscript{2} showed distinct piezoresponses. The piezoelectric coefficient \(d_{11}\) was calculated based on the slope of the lateral PFM result and found to be 3.14 ± 0.3 pm/V for pristine MoS\textsubscript{2} and 3.57 ± 0.2 pm/V for Au-doped MoS\textsubscript{2} respectively. This means that the piezoelectric constant value of pristine MoS\textsubscript{2} is less than the theoretical value due to the formation of extra carriers caused by defects, whereas the value for Au-doped MoS\textsubscript{2} is close to the theoretical piezoelectric constant due to the effective control of the extra carriers.

The output change was confirmed through PENG fabrication and a bending test. Fig. 3c and 3d show the piezoelectric output currents and voltage responses of pristine MoS\textsubscript{2} and Au-doped MoS\textsubscript{2}. The fabrication process for the PENG device for measuring piezoelectric output and the strain calculation are detailed in the Supporting Information and Fig. S10. The short-circuit current was measured under 0.48 \% strain and 50 mm/s strain rate, and the output voltage was measured with a load resistance of 1 G\textOmega, respectively. As can be seen in Fig. 3c, the current output of the Au-doped MoS\textsubscript{2}-based PENG produced about 100 pA, which is more than two times higher than that of pristine MoS\textsubscript{2} (about 42 pA). The output voltage of Au-doped MoS\textsubscript{2} was more than three times (30 mV) higher than that of pristine MoS\textsubscript{2} (10 mV), as shown in Fig. 3d. The switching polarity test indicated that the output current and voltage of the PENG devices occurred in the pristine and Au-doped MoS\textsubscript{2} rather than the measurement system noise (Fig. S11). To get more confidence, PENG was fabricated by depositing electrodes on a PET substrate without MoS\textsubscript{2}, and the output was checked, no output appeared without MoS\textsubscript{2} shown in Fig. S12.

In order to provide an understanding of strain effects on the WF, we performed a DFT calculation of MoS\textsubscript{2} and Au-doped MoS\textsubscript{2} with strain imposed. Fig. 4a shows the changes in the
WF, Fermi level, and vacuum level of pristine MoS$_2$ and Au-doped MoS$_2$ when strains of -0.10 to 0.10 are applied. The WF of MoS$_2$ remains constant, even when strain is imposed on the MoS$_2$ layer. The Fermi level monotonically decreases when tensile strain is applied. In contrast, the Fermi level increases under compressive strain. Simultaneously, the vacuum level moves in the same direction, so that the overall work function behavior remains constant. It is results of linear changing of the electrostatic potential as shown in Fig. S13. The central symmetry potential profiles in MoS$_2$ layer linearly decrease when compressive strain was applied. In the vacuum space, electrostatic potentials show opposite trends, which overall potential changing was also reduced under compressive strain. In the case of Au-MoS$_2$, the linear change in the WF shows as strain is imposed, although the Fermi level shows relatively smaller changes. In contrast, the vacuum level is greatly shifted when strain is imposed. The doped Au contributed to non-axis symmetry potential profiles at near 0.45 fraction coordinate and overall electrostatic potential changes are also reduced.

To further understand the effect of strain on pristine MoS$_2$ and Au-doped MoS$_2$, the charge density differences under strains ranging from -0.1 to 0.1 % were compared. In the case of pristine MoS$_2$, when a defect occurs at the S site, S is attached again, and the electron distribution changes (Fig. S14 and S15). It can be seen that the overall electron redistribution occurs over a wide area, and when negative strain is applied, there is a difference in shape, but it does not show a relatively large change.

On the other hand, the difference in charge density when strain is applied to Au-doped MoS$_2$ shows a clear difference. Fig. 4b shows the charge density difference when strain is imposed on Au-doped monolayer MoS$_2$. The difference in charge density of Au-doped MoS$_2$ was calculated within the strain range from -0.1 to 0.1 % and implemented as a 3D image. Note that Au-doped MoS$_2$ has excess charge between Mo-Au bonding with electron deficiency at the top
of Au. When tensile strain is applied, the electron deficiency is reduced (Fig. S16 and S17), and the bottom-most part of the MoS$_2$ shows excess charge in the form of electrons, as shown for $\varepsilon = 0.10$ in Fig. 4b. This implies that electrons transfer from Mo and Au to S and can move easily. Under compressive strain, the electron deficiency on the Au above increases (Fig. S16 and S17), and a neutral electron configuration was observed at the bottom surface of MoS$_2$, shown for $\varepsilon = -0.10$ in Fig. 4b.

In summary, improvement and prediction of the piezoelectric properties of Au-doped monolayer MoS$_2$ through our DFT calculations and experimental results have been verified. We confirmed that Au is an effective doping element by calculating the WF changes when various metal elements, Au, Ag, Pt, and Al, were considered. In addition, we have presented calculation results comparing the WF and charge density changes for pristine MoS$_2$ and Au-doped MoS$_2$ when strain was applied, providing an understanding of the effect of the electronic structure of doped MoS$_2$ on the piezoelectric properties.

Acknowledgements

This work was financially supported by Basic Science Research Programs (2021R1A2C2010990) through the National Research Foundation of Korea (NRF) funded by Ministry of Science and ICT. This research was also supported by the Chung-Ang University Research Grants in 2022.

References


Fig. 1 Density functional theory (DFT) calculation results on the change in work function (WF) when various novel metals (Au, Ag, Pd, Pt, and Al) are doped onto monolayer MoS\textsubscript{2}. (a) Structure of monolayer MoS\textsubscript{2} and three-dimensional (3D) charge density difference. (b) Calculated results on the vacuum level and Fermi level changes according to the metal doping. (c) The bar graph shows the WF values when each element is doped onto MoS\textsubscript{2}, based on DFT calculations and compared with pristine MoS\textsubscript{2}. 
Fig. 2 Experimental results showing the work function (WF) change of monolayer MoS$_2$ before and after Au doping. (a) Atomic force microscope (AFM) topographical images. (b) Kelvin probe force microscope (KPFM) mapping images showing the Fermi level change. (c) X-ray photoelectron spectroscopy (XPS) peaks of Mo 3d.
Fig. 3 Evaluation of the piezoelectric properties of Au-doped MoS$_2$. (a) Photograph of actual piezoelectric nanogenerator (PENG) device, line profile image of monolayer MoS$_2$, and detailed structure of the PENG on a flexible substrate. (b) Piezoresponse as a function of the magnitude of external bias applied to $\alpha$-quartz, pristine MoS$_2$, and Au-doped MoS$_2$, with the inset showing the piezoelectric coefficient $d_{11}$ for these materials. (c) Piezoelectric current output. (d) Piezoelectric voltage output.
Fig. 4 Calculation result showing electronic band structure change when strain is applied to pristine MoS$_2$ and Au-doped MoS$_2$. (a) Changes in the work function, Fermi level, and vacuum level when strain in the range of $-0.1 - 0.1$ % is applied. (b) 3D image showing the calculated results for the charge density difference when strain is applied to Au-doped MoS$_2$. 
Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: