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AuNx stabilization with interstitial nitrogen atoms: A Density Functional Theory Study

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Abstract. Researchers have been studying 4d and 5d Series Transition Metal Nitrides lately as a result of the experimental production of AuN, PtN, CuN. In this paper, we used the Density Functional Theory (DFT) implementing a pseudopotential plane-wave method to study the incorporation of nitrogen atoms in the face-centered cube (fcc) lattice of gold (Au). First, we took the fcc structure of gold, and gradually located the nitrogen atoms in tetrahedral (TH) and octahedral (OH) interstitial sites. AuN stabilized in: 2OH (30%), 4OH and 4TH (50%), 4OH – 2TH (close to the wurtzite structure) and 6TH (60%). This leads us to think that AuN behaves like a Transition Metal Nitride since the nitrogen atoms look for tetrahedral sites.

Key Words: Crystal Structure, Point Defects, Solid Solutions, Computer Simulation, Superlattices, Nitrides.

1. INTRODUCTION

Transition Metal Nitrides (TMN) are hard materials which are resistant to wear, have high melting points and good thermic stability. They have a significant number of applications in cutting tools, resistant surfaces, semiconductors, or conductivity among others [1-5]. Long time ago (approx. 50 years), the most studied nitrides were 3d series interstitial nitrides [6-9], but after the experimental production of some TMN as Ag_xN, Au_xN, Pt_xN, C_xN in these last ten years, they begun to study strongly 4d and 5d Series Transition Metal Nitrides (Ru, Rh, Pd, Ag, Os, Ir, Pt, and Au) [10-14]. It is interesting to know that these noble metals are part of new TMN family (IrN_2, AgN_2, AuN_2, PtN_2) in which nitrogen atoms settle themselves into interstitial sites of the fcc structure of a metal [15]. Authors as Yu, Kanoun, Zhao, and Mohammed have conducted research on these types of nitrides [16-19]. Zhao considered six structures (Rocksalt, Zinc Blenda, CsCl, WurtZite, NiAs, and WC) using first principle methods to study the electronic and structural properties of nitrides from LaN to AuN. The most stable structures found were Rocksalt for LaN, HfN and AuN, WC for TaN, NiAs and Wurtzite for ReN, OsN, IrN and PtN. They are metallic structures and have covalent bonds. The pressure produced between 5 to 40 GPa demonstrated that as coatings these nitrides may potentially become super hard materials. Kanoun confirm conductive nature and found Rock Salt structure to be the most stable for AuN using DFT [17]. Yu observed the structural stability of this family in fluorite-type structures (IrN_2, PtN_2 y AuN_2) and reported that nitrogen atoms fill in the interstitial sites of a metal structure [15]. Mohammed identified that the most stable form of gold nitride is Au_3N using DFT, his report is based in the comparison of 20 structures between Au_3N, Au_2N and AuN, and observed the phase Au_2N has lower symmetry than phase Au_3N (D09) [20]. Due to the difficulty these nitrides have had being synthetized, there is little research work on their experimental production. The problem today is that we do not know in what phase they are in, so this has led to a lack of databases for most of them for X-Ray Diffraction (XRD); just in the

XRD we found, one can not find notable differences with the ones found for a lattice of pure metal. This is mainly because the structures have the same metal sub-lattice, and in heavy-atom metal dispersion, they are predominant in X- Ray Diffraction (XRD) pattern intensity [16]. By means of ab–initio pseudopotential calculations, Siller has shown a triclinic structure for an Au_3N phase [11]. For XRD, it is observed an approximate 0.1 % dilatation for the fcc structure of Au incorporating Nitrogen atoms, and obtained AuN using techniques as ion sputtering and plasma etching as solid solutions [10, 21]. Quintero reported a species of $AuN_{0.6}$ in an N1s at 398.1 eV narrow spectrum as the first AuN film produced using a pulsed arc technique [13, 22]. In this paper, we present the incorporation of nitrogen atoms to the fcc structure of gold by means of DFT, at interstitial sites (OH and TH). Nitrogen atoms were gradually introduced in ranks of 30, 50 and 60 %, to observe if gold nitride has a TMN behavior, for different M_xN_y (M: Metal, N: Nitrogen) compositions, that lead to mononitrides production with different structures. The most common and important MN, has a basic fcc structure. M_2N nitrides follow it in importance, and they are usually found in hexagonal close packing (hcp), and rhombohedral and orthorhombic structures are formed where there is a larger amount of nitrogen than of a metal [23]. Finally, we determined the possible interstitial sites that nitrogen atoms may take in an fcc gold lattice.

2. COMPUTATIONAL DETAILS

Nitrogen positions in a cubic Au lattice were determined theoretically based on DFT. Energy calculations were conducted using the pseudopotential plane-wave method. The exchange and correlation effects were treated with a Generalized Gradient Approximation (GGA) implemented in Perdew-Wang approximations (PW91) [24]. We used ultrasoft pseudopotentials where states 5d for gold were introduced as valence electrons [25]. Calculations were developed using a QUANTUM-espresso simulation packet [26]. Electron wave functions were expanded up to a cutting energy of 35, and 420 Ry for electronic density. We used a 10×10×10 k-point grid centered on Γ for an irreducible Brillouin zone sampling in the special Monkhorst–Pack schema [27]. We adopted Methfessel-Paxton technique with a 0.02 Ry width value for smearing [28]. Those parameters assure a convergence for total energy close to 5 meV. Since fcc structures have eight octahedral sites (OH) and four tetragonal (TH) sites (Fig 1), different structure configurations were taken for different nitrogen concentrations within the fcc gold lattice. When four nitrogen atoms fill the OH sites (Fig. 1b), which are 6-coordinate, the structure presents a point symmetry of 4/m 3* 2/m. In this notation, '4' stands for the presence of 4-fold rotation axes, 'm' stands for mirror planes, '2' stands for 2-fold rotation axes, and '3*' stands for 3-fold rotoinversion axes. When eight nitrogen atoms are located in the TH sites, which are 4-coordinate, the structure takes also a symmetry 4/m 3* 2/m. In this work, we have located different number of N atoms in the possible OH and TH sites and DFT relaxations were performed by fully relaxing the coordinates of the atoms until the forces were smaller than 0.1 eV/Å. In addition, we resolved Kohn-Sham equations via a self-consistent approach for different volumes generating a characteristic Energy vs Volume curve for each configuration, and we were able to observe how this new TMN stabilizes for different configurations and concentrations.

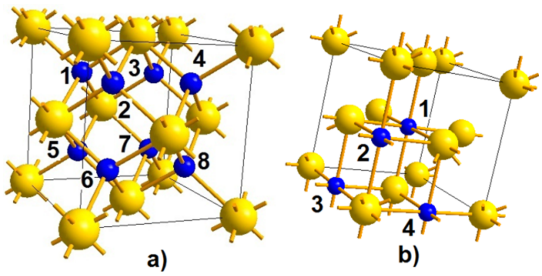

Figure 1. Positions of the interstitial sites, a) Tetrahedral Sites and b) Octahedral Sites.

3. RESULTS AND DISCUSION

For a structural study, we adjusted the energy curves against volume (see figure 2) using Murnaghan's equation of state [29]; and this way, we found a lattice parameter (a), an equilibrium volume (V_0) and a volume module (B). The values found in the fcc gold structure were: a=4.15 Å, V_0=120.6 Å and B=1.73 Mbar, which were very close to the experimental parameters, a=4.08 Å and B=1.70 Mbar. Thus, our result slightly overestimates the experimental values by ~1.7%. In figure 1, one can see the fcc gold structure used as a base to introduce nitrogen atoms in interstitial sites, and later it was easy to determine the structural parameters of each proposed phase. As a result of the different concentrations of nitrogen atoms and of the interstitial positions of a cubic gold lattice, the possible configurations studied are listed on table 1, and figure 3 are shown the most stable structures for 30, 50 and 60 %. Then, for each structure, we found total energy, total force and stress for each of the previously mentioned configurations in order to determine the most stable positions (minimum energy and zero total-force) of the interstitial sites nitrogen atoms take (Table 1).

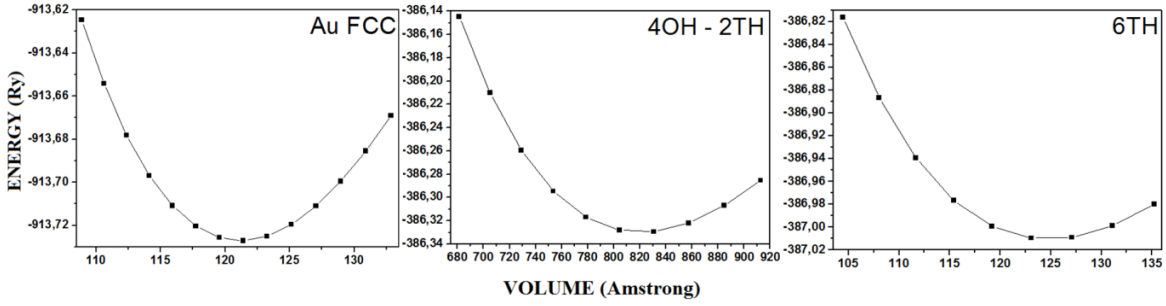

Figure 2. Energy vs Volume Curve for Au-fcc, 4OH–2TH and 6TH structures.

In table 1, nitrogen atoms prefer OH interstitial sites for low nitrogen contents because for 30% of the most stable configuration is 2OH (minimum energy and zero total-force, see figure 3a). For configurations belonging to 50%, the most stable 4OH and 4TH do not present any considerable difference; nevertheless, configuration 4OH presents a slightly lower energy (figure 3b). Zhao et al reported a similar behavior for others TMN [18]. In the literature, one can find that the most stable structure for AuN is rock salt (OH sites) followed in order by zinc blenda, CsCl and wurtzite structures, which have a small energy differences among them [19]. Therefore, it is observed that when nitrogen concentration increases, after the octahedral site are occupied, nitrogen atoms locate into tetrahedral sites trying to imitate the tetrahedral symmetry as it is found in the wurtzite structure [19].

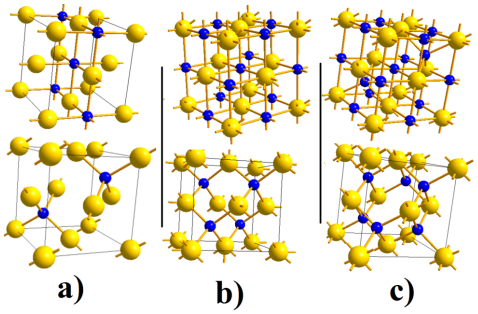

Figure 3. Configurations more stable. a) 30%, b) 50% and c) 60%

For a 60% concentration, the most stable result corresponds to configurations 4OH–2TH and 6TH; in the ones with zero total-force, configuration 4OH–2TH presents minimum energy (figure 3c). For configurations 4OH–2TH and 6TH, we performed lattice relaxation by means of E vs V (figure 1), and determined that the most stable configuration is 6TH. These data agree with what was reported for the TMNs, for they present cubic structures in a range of 30 at 70% [22, 30]; besides, this behavior shows that AuN behaves as a TMN, for when it exceeds this concentration, it may have a phase transition to hexagonal close packing (HCP).

Table 1. Configurations for nitrogen atoms in the Au-fcc structure.

% Nitrogen Atoms		**Configuration**	**OH site**	**TH site**	**Energy (Ry)**	**Total Force (Ry/a.u.)**	**Stress (kbar)**
30%	a	1 OH – 1 TH	5	1	-307.210	0.784	996.29
	b	**2 OH (top fig 3a)**	1, 4	-	**-307.579**	**0**	**646.91**
	c	2 TH	-	5, 7	-307.070	1.131	1179.01
		2 TH	-	5, 3	-307.154	0.825	1174.78
		2 TH (down fig 3a)	-	5, 4	**-307.410**	**0**	**1121.13**
50%	a	**4 OH (top fig 3b)**	1, 2, 3, 4	-	**-347.331**	**0**	**-197.16**
	b	**4 TH (down fig 3b)**	-	6, 1, 7, 4	**-347.312**	**0**	**295.41**
60%	a	1 OH – 5 TH	1	1, 4, 5, 6, 7	-383.296	0,745	3863.15
	b	2 OH – 4 TH	1, 4	6, 1, 7, 4	-383.115	0,453	3803.98
		2 OH – 4 TH	2, 4	6, 1, 7, 4	-383.115	0,453	3804.00
	c	3 OH – 3 TH	2, 3, 4	3, 4, 5	-383.706	0,901	3421.89
	d	4 OH – 2 TH	1, 2, 3, 4	5, 7	-383.783	1,376	3246.57
		4 OH – 2 TH	1, 2, 3, 4	5, 3	-383.842	1,058	3213.93
		4 OH – 2 TH (top fig 3b)	1, 2, 3, 4	5, 4	**-384.213**	**0**	**3029.81**
	e	6 TH	-	1, 3, 4, 5, 6, 7	-383.662	0,852	3862.94
		6 TH (down fig 3c)	-	1, 3, 4, 5, 6, 8	**-384.148**	**0**	**3637.94**

Yu et al reported that new TMN families, among which we can find AuN, are structures that prefer tetrahedral sites for concentrations over 50% [15]. In the literature, Siller and Quintero show that nitrogen is found interstitially in the fcc structure of gold, althoug XRD analysis do not show any parameter changes in a gold lattice [21, 31, 32]. In that case, DFT results without relaxation present a 4.15Å lattice parameter which is close to the one Devia observed experimentally (4.08 Å fcc gold lattice). Also, after structural relaxation, the lattice parameters increase up to 4.956 Å (for configuration 4OH-2TH) and 4.664 Å (for configuration 6TH). Since lattice parameters are quite similar to the results obtained experimentally [31,32], we could think that the structure obtained experimentally could correspond to configuration 4OH–2TH without relaxation, and this is very close to a rock salt structure (figure. 3c).

4. CONCLUSIONS

We used Density Functional Theory (DFT) calculations in order to analyze nitrogen atom interstitial incorporation into the cubic fcc lattice of gold. Results indicate that these nitrogen atoms prefer lattice tetrahedral sites as it happens for any TMN. Configurations 4OH–2TH and 6TH were the most energetically-stable structures for AuN when it has 60 % nitrogen atoms. However, for higher N concentrations, nitrogen atoms locate in each of tetrahedral sites, tending to generate the wurtzite hexagonal lattice. Finally, lattice parameters found are quite similar to the ones obtained experimentally, in addition, when the nitrogen is incorporated in the Au structure, relaxed parameters increase abruptly. Our results provide a consistent interpretation of the experimental data and could be used for understanding the growth of gold nitride. Therefore, from the results obtained in this research, it

is expected that AuNx compound could be used in research aimed at the future development of new materials and the design of electronic devices.

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