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# Influence of boat material on the structure, stoichiometry and optical properties of gallium sulphide films prepared by thermal evaporation

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## HIGHLIGHTS

- Gallium sulphide films are prepared by thermal evaporation from a Mo or Ta boat.
- Mo-boat prepared pristine film has Ga and S in 1:1 atomic ratio and is transparent.
- Ta-boat prepared pristine film is Ga rich and absorbing.
- Mo/Ta-boat prepared films crystallise into $Ga_2S_3$/GaS on vacuum annealing.
- Diffusion of gallium in glass on vacuum annealing improves transmission of films.

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## ABSTRACT

The paper describes the deposition of thin films of gallium sulphide on soda-lime glass substrates by thermal evaporation of chemically synthesized powders consisting of gallium sulphide and gallium oxyhydroxide from a Mo or Ta boat and the evolution of their compositional, structural and optical properties on vacuum annealing. The films deposited from Mo or Ta boats possessed distinctly different properties. The Mo-boat evaporated pristine films were amorphous, transparent ($\alpha \sim 10^3$ cm$^{-1}$) in visible region and had a direct band gap of about 3.2 eV. Vacuum annealing at 723 K brought about their crystallization predominantly into cubic $\gamma$-$Ga_2S_3$ and a blue shift by about 0.2 eV. The Ta-boat evaporated pristine films were also amorphous but were absorbing ($\alpha \sim 10^4$ cm$^{-1}$) and had a direct band gap of about 2.1 eV. These crystallized into hexagonal GaS and experienced a blue shift by more than 1.0 eV on vacuum annealing at 723 K. The dissimilar properties of the two kinds of films arose mainly from their different atomic compositions. The Mo-boat evaporated pristine films contained Ga and S in ~1:1 atomic proportions while those prepared using Ta-boat were Ga rich which impaired their transmission characteristics. The former composition favoured the stabilization of S rich gallium sulphide ($Ga_2S_3$) phase while the latter stabilised S deficient species, GaS. Besides inducing crystallization, vacuum annealing at 723 K also caused the diffusion of Ga in excess of atomic composition of the phase formed, into soda-lime glass which improved the optical transmission of the films. Gallium oxyhydroxide, an inevitable co-product of the chemical synthetic process, in the evaporant introduced oxygen and hydrogen impurities in the films which do not seem to significantly influence their optical properties.



## 1. Introduction

Group III oxide and chalcogenide semiconductors are promising materials for photovoltaic and optoelectronic applications due to their interesting electrical and optical properties [1,2]. Gallium oxide ($Ga_2O_3$) and gallium sulphide are the typical representatives of the Group III oxide and chalcogenide families respectively. $Ga_2O_3$ has five polymorphs. It occurs in monoclinic β phase under ambient conditions. The other polymorphs are formed at higher temperatures. β-$Ga_2O_3$ is a wide band gap (5.0 eV) intrinsic insulator but acquires n-type conductivity on doping. As a result, it can serve as an ultraviolet transparent conducting oxide for flat panel displays and solar cells. Intrinsic β-$Ga_2O_3$, on the other hand, has applications in semiconducting lasers and field effect devices and is also used as an anti-reflecting coating.

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Gallium sulphide exists in two stoichiometric formulations: gallium monosulphide (GaS) and gallium sesquisulphide ($Ga_2S_3$). Both types of gallium sulphide exhibit polymorphism with β-GaS (hexagonal) and α-$Ga_2S_3$ (monoclinic) being the most stable polymorphs under normal conditions. GaS has, similar to graphite, a layered structure. A strong covalent interaction exists within the layers which, in turn, are bonded by weak van der Waals forces [2]. The layered structure imparts anisotropicity to the functional properties of the material. Gallium sulphide is probably one of the least studied compounds in the III–VI chalcogenide family, however, the unique structure of GaS has evoked considerable interest among the researchers in recent years. In terms of optical characteristics, GaS has a direct band gap ($E_g$) of about 3.0 eV and an indirect $E_g$ of about 2.6 eV [3]. It exhibits, depending on composition, n-type or p-type conductivity. Ga-rich GaS is an n-type and S-rich GaS is a p-type semiconductor [4]. On the other hand, $Ga_2S_3$ has a direct $E_g$ of about 3.5 eV and exhibits p-type conductivity [5]. In view of rather large $E_g$, gallium sulphide is a candidate material for buffer layers in a photovoltaic cell. GaS provides effective surface passivation to GaAs and has been shown to enhance its photoluminescence yield by two orders of magnitude [6]. It is also being investigated for the fabrication of near-blue-light emitting devices [7].

Thin films of gallium sulphide have been prepared by several methods that include metal-organic chemical vapour deposition (MOCVD) [5,8], modulated flux deposition [9,10], microwave glow discharge [11], reactive RF sputtering [3] and molecular beam epitaxy [12]. MOCVD has, in fact, been used to prepare GaS or $Ga_2S_3$ films using suitable precursors. However, in this technique the crystallinity of the films is strongly affected by the nature of the substrate and deposition temperatures [5,8]. The films prepared by modulated flux deposition, on the other hand, were amorphous and possessed Ga rich composition. Moreover these contained up to as high as 34 at.% oxygen, suggesting the formation of essentially ternary $GaS_xO_y$ films [9]. The GaS films prepared by microwave glow discharge also contained up to 5 at.% oxygen as an impurity [11]. Interestingly, recently Chowdury and Ichimura have reported the deposition of $GaS_xO_y$ films by photochemical deposition (PCD) and electrochemical deposition techniques [13,14]. $GaS_xO_y$ films, like gallium sulphide films can be used as buffer layers in photovoltaic devices. The films reported in these studies contained only 5–18 at.% S signifying difficulties in its incorporation in the films by photochemical or electrochemical reactions.

In the present paper we report our investigations on the preparation of gallium sulphide films by the thermal evaporation of chemically co-precipitated gallium sulphide and gallium oxyhydroxide (GaOOH) powders from a Mo or Ta-boat. The effects of vacuum annealing on the compositional, structural and optical properties of the films have also been probed. These investigations form a part of our current studies on the development of metal sulphide films for photovoltaic applications by the resistive evaporation of chemically synthesized sulphide powders. The synthesis of pure gallium sulphide powders, unlike those of copper or indium sulphide, by precipitation reaction in aqueous medium is difficult due to the propensity of gallium salts to undergo hydrolysis. Meanwhile the choice of thermal evaporation based on that the fact that it is a simple yet an effective technique for the deposition of elemental as well as compound films. It has been previously employed for the deposition of GaS films using GaS crystals as evaporants but the preparative method and the chemical composition of the films were not described in detail which prompted us to undertake the present investigations [15]. It is to be noted that these are important considerations in view of the fact that the optical properties of the films, as observed in current study, depend on the preparative conditions, particularly on the type of boat material used for evaporation. Furthermore, an assessment of oxygen content of the films is desirable since gallium sulphide films often contain, for reasons not explained, oxygen as an impurity in fairly large concentrations [9,11]. Presently, the composition of the films has been comprehensively examined by ion beam analysis techniques with particular emphasis on the analysis of hydrogen and oxygen, and an attempt has been made to correlate it with the structural and optical properties of the films.

## 2. Experimental details

### 2.1. Chemical synthesis of evaporant

Gallium sulphide was synthesized by co-precipitation method using sodium sulphide as the precipitating agent. The procedure involved the addition of 50 mL of 1500 mM sulphide solution to 250 mL of 190 mM gallium chloride solution in ambient conditions. The precipitation was slow and therefore the solution was aged overnight for complete precipitation. The precipitate was filtered and washed copiously initially with deionised water and subsequently with isopropanol. It was later dried under the flow of argon at 383 K for 2 h. The dried powder was used as an evaporant for the deposition of films.

### 2.2. Deposition of films

The films were deposited on soda lime glass substrates at a rate of 1–2 Å/s by resistively heating the evaporant in a Mo-boat or Ta-boat at ~$3 \times 10^{-4}$ Pa vacuum in a thermal evaporation unit. Both Mo and Ta boats had a rating of 200 A and weighed ~1.63 g and 2.34 g respectively. Vacuum in the deposition chamber was created and maintained by an oil diffusion pump backed by a rotary pump. The substrates were initially cleaned chemically and were subsequently sputter cleaned *in situ* in Ar plasma. The distance between the boat and the platen onto which the substrates were fixed was about 70 mm. The platen rotated at 25 rpm to ensure uniform deposition. Though the substrates were not intentionally heated, their temperature rose to ≤323 K at the end of the depositions. The temperature of the substrates was measured by a thermocouple held close to the platen. Films of three different thicknesses namely ~130 nm, 280 nm and 390 nm were deposited by evaporation from Mo boats. These are referred to as Mo1, Mo2 and Mo3 films respectively. Similarly 150 nm, 230 nm and 280 nm films, referred to as Ta1 Ta2, Ta3 films respectively, were deposited by evaporation from Ta boats. The thicknesses of the films were determined by Rutherford backscattering spectrometry (RBS) with a precision of ~5%. A number of films of were deposited in a run. The thickness of these films varied within ±10%. Subsequent to their deposition the films were annealed in vacuum in a quartz tubular furnace in 523 K–723 K temperature range for 4 h. The vacuum during annealing, created by a turbomolecular pump was better than $7 \times 10^{-3}$ Pa.

### 2.3. Characterization

#### 2.3.1. Phase analysis

The phase evolution in the films was examined by glancing-incidence X-ray diffraction (GI-XRD) (incidence angle = 2°; step size = 0.1°; scan speed = 1° per minute) by a Rigaku (Ultima IV) diffractometer using Cu $K_\alpha$ radiation ($\lambda$ = 1.5402 Å). The same instrument was used to analyse residues in Mo or Ta boat in powder mode.

#### 2.3.2. Compositional analysis

*2.3.2.1. Determination of atomic ratio of Ga, S and O by backscattering spectrometry.* Films, pristine as well as those vacuum