1.1 Introduction

Soft and hard x-rays regions of the electromagnetic spectrum offer great opportunities in both basic science and applications based on the technology developed [1]. Various applications are demonstrated in many fields using electromagnetic radiation. For example, the applications include that these regions of electromagnetic spectrum allow one to see smaller features in microscopy and write finer features in lithography. However, while using electromagnetic radiation, it is required to either focus or redirect the radiation, for which one needs optical components such as lenses or mirrors.

Lenses or thin film coated mirrors which come under the category conventional optical elements are not useful for the of x-rays range as refractive index corresponding to these wavelengths is small as compared to vacuum and hence gives negligible refraction. Whereas, the use of thicker lenses is also not acceptable for getting noticeable refraction because of the absorption. Therefore the field of multilayer coating has become an important area for using soft and hard x-rays in the focusing and imaging optics. However, as discussed the coming section, the x-ray are reflected below the critical angle of incidence, wavelength dispersion with high spectral resolution can only be achieved by specifically designed mirrors at higher angles. Because of this reason, usually multilayer mirrors are formed by depositing alternating layers
of two materials of dissimilar refractive indices, which are considered to form a long-term stable interface. Such multilayer mirrors, consisting two materials of dissimilar refractive indices are shown to find various application viz., as x-ray monochromator, optical elements in x-ray regime for manipulate x-ray beams in laboratory as well as synchrotron radiation sources [2, 3]. The details description of the multilayer mirror will be discussed in the next section.

1.2 X-ray optics

The electromagnetic radiations of energy range between 0.1 to 100keV are called x-ray. They are on shorter wavelength side of visible electromagnetic radiation. X-rays are resultant of electron transition from higher energy state to lower energy state in an atom, when the inner orbital electron gets knocked off by external radiation [4]. The wavelength of x-ray radiation ranges from 0.01 to ~23 nm. X-rays with a wavelength longer than 0.1 nm are called soft x-rays and wavelengths shorter than this are called hard x-rays. The wavelength range of 30 nm to 200 nm corresponds to the vacuum ultra violet (VUV) region. Soft x-rays and VUV wavelengths are strongly absorbed in the atmosphere and therefore, need vacuum for the experimentation which make the instrumentation more complicated as compared to that for hard x-rays [5, 6].

1.2.1 Refractive optics

The refractive index is close to unity for x-rays and absorption is strong and therefore, the usual refractive optics cannot be used for describing the soft x-rays refraction as the conditions for soft x-rays are quite different compared to visual optics. As a result of this lenses should be very thick to create any noticeable refraction. But all the radiation will be absorbed in that case due to highly absorbing nature of soft X-rays.
1.2.2 Reflective optics

The reflected amplitudes s polarization \((r_s)\) and p polarization \((r_p)\) depend on the grazing angle of incidence \(\alpha_1\) and the relative complex reflective indices. According to the Fresnel equations [7]:

\[
\begin{align*}
    r_s &= \frac{\sin \alpha_1 - \sqrt{n^2 - \cos^2 \alpha_1}}{\sin \alpha_1 + \sqrt{n^2 - \cos^2 \alpha_1}} \\
    r_p &= \frac{n \sin \alpha_1 - \sqrt{n^2 - \cos^2 \alpha_1}}{n \sin \alpha_1 + \sqrt{n^2 - \cos^2 \alpha_1}}
\end{align*}
\]

where \(\alpha_1\) is the grazing angle and \(n = n_2/n_1\) are the refractive indices of the refracting and incident media respectively. The reflectivity is then calculated using:

\[
R = rr^* ,
\]

where \(r^*\) is the complex conjugate of \(r\).

![Figure 1.1: Calculated reflectivity of s-polarized radiation with a wavelength of 4.4 nm on a W mirror.](image)

Figure 1.1 shows the calculated reflectivity for a W mirror considering the s-polarized radiation with a wavelength of 4.4 nm. From this graph it is clear that the reflected intensity at all but very grazing angles is low. The major part of the radiation is absorbed in the tungsten mirror. Therefore, to increase the reflectivity beyond what is obtainable using a single surface, it is attempted
to reflect the transmitted radiation again before it is absorbed in a given structure. A multilayer mirror is actually based on this principle, and the following section deals with the theory of a multilayer mirror [6].

1.3 Theory of x-ray multilayer mirror

One can define the multilayer mirror as a stack of layers of two or more alternating materials, in which one has a low refractive index and the other material has a high refractive index. One such structure consisting of two layers (shown as A and B) is shown in figure 1.2. The incident radiation is reflected at each interface between the two materials, as shown in the figure 1.2 and the remaining part is transmitted. At the first interface (vacuum/high δ) internal reflection occurs, which is due to the fact that the refractive indices (n = 1- δ - iβ, where typically the values of δ, β are of the order of 10⁻⁵ for hard x-rays and 10⁻³ for soft x-rays ) for x-rays of nearly all materials are below one. This is in opposite to the case of visual light. At the next interface (high /low δ) external reflection occurs. This also adds an additional phase shift of 180º to the reflected radiation.

Depending on the layer thickness values, all reflected radiation will add up in phase resulting in diffraction maxima. This is possible, when the thickness d of each period (the combination of two layers) satisfies the Bragg equation:

\[ n\lambda = 2d \sin \theta, \]  

where n is an integer number representing the Bragg order and θ is the incident angle of the radiation.

From the above stated Bragg equation it is also clear that a given multilayer mirror is a dispersive element. That means, each wavelength is only reflected at one particular angle, for a given Bragg order. However, this assumes an infinite number of periods, which is practically not feasible. As a result of this, limited number of periods, a specific wavelength is reflected at a small angular range
Δθ. Therefore, reflectivity R and its angular selectivity \( \theta/\Delta \theta \) are the parameters which are used to characterize a given mirror. Alternatively, one can select a fixed angle, and look at the wavelength range \( \Delta \lambda \) reflected at this angle, which is usually expressed as a wavelength selectivity \( \lambda/\Delta \lambda \) [6, 8].

![Figure 1.2: Principle of a multilayer mirror.](image)

### 1.3.1 Recursive method

Generally, recursive calculation methods are used to calculate the actual reflectivity of any structure [9]. In this method, the total reflected amplitude \( r_f \) of a film on top of another structure is determined by the reflected amplitude \( r_t \) of the top interface and the reflected amplitude \( r_b \) of the bottom structure:

\[
r_f = \frac{r_t + r_b e^{2i\phi_i}}{1 + r_t r_b e^{2i\phi_i}} \tag{1.5}
\]

where \( \phi_i = \frac{2\pi}{\lambda} n_i d_i \sin \alpha_i \)

represents the phase delay produced by the propagation of the wave through the \( i^{th} \) film with a thickness \( d_i \) and a refractive index \( n_i \). \( \alpha_i \) is the (grazing) angle of the wave within this layer, to be calculated using Snell’s law. The reflected amplitude \( r_b \) of the bottom structure can be recursively calculated by sub-dividing this structure in another layer on top of the remaining structure, until
only one layer on top of the substrate remains. In this last iteration $r_b$ equals the Fresnel reflectivity of the substrate. This method includes the influence of absorption by means of the complex part of the refractive index ($n_i$), therefore, it gives the exact solution for structures that can be described using sharp boundaries between all layers [6].

### 1.4 Multilayer Structure for Soft X-ray Optics

For the good multilayer mirrors the following are the requirements that one needs to keep in mind while designing:

1. Refractive index contrast at the interfaces
2. Minimal absorption in the low-Z material.
3. Thin high-Z layer.
4. Interfaces which are chemically stable with time.
5. Minimal inter-diffusion at the interface.
6. Minimal interfacial roughness (no crystallite formation within the layers, no shadowing in the coating process, surface mobility)
7. Thermal stability during illumination.
8. Chemically stable vacuum interface (e.g., SiO$_2$, or capping layer)

Each of the above point is crucial in making the mirrors. Like the control of the inter-diffusion at the interfaces and the uniform thickness during the deposition are the major hurdles in making the mirrors experimentally. For any practical use of such multilayers, long terms stability of their properties is also very important and a prerequisite. Any interdiffusion at the interfaces of the constituent layers can severely deteriorates the reflectivity at Bragg peak, resulting in loss of reflected intensity. On the other hand any change in the density of layers associated with defect annihilation, phase formation at the interfaces etc can result in a shift in the position of the Bragg peak, which is essentially because of change in the thickness of the multilayer. Any such shift
in the position of the Bragg peak is an unwanted thing in their practical use. For example, when using such mirrors (which are basically designed for a particular wavelength) in the beam lines the shift of the Bragg angle can result in difficulties in achieving the focusing on the sample etc.

1.5. Review of earlier work

The beginning of the successful deposition of multilayer structures dates back to 1935 [10], in which the researchers deposited multilayers of gold and copper with periods of approximately 100 Å. The major problem faced was of metallurgical instability with the two components inter-diffusing over a period of weeks.

However, the field remained inactive till 1960’s and the activity began after the work of Dinklage et al. [11] who have reported the study of multilayers of Pb/Mg, Au/Mg and Fe/Mg with the periods of 3 to 5 nm. It is reported by Dinklage et al. [10] that the Fe/Mg multilayers were stable at leaser for one year as compared to Pb/Mg and Au/Mg. This work has motivated lot of researchers to explore the physical and chemical properties of the constituent elements forming the multilayer structures and to address the issue of stability with time. Coming to the field of X-ray optics, the work received attention after the work of Spiller [12] in 1972, who has reported the study of heavy/light materials in the form of quarter-wave stacking’s and shown that these structures can be used as efficient reflectors at near-normal incidence. The multilayers studied by Spiller et al., were prepared by vapour deposition technique. The study of multilayers prepared with sputtering began in 1976 after the work of Barbee and Keith [13]. The work of Barbee et al., was immediately followed by many research worker across the world in the study of multilayers consisting light / heavy elements as X-ray optics. In recent times, many deposition techniques such as MBE (molecular beam epitaxy), laser ablation (PLD), ion beam sputtering (IBS) etc., with their own
advantages / disadvantages were used to prepare the multilayers for the study of x-ray optics [14, 15]. Similarly various characterization techniques such as x-ray reflectivity (GIXR), x-ray diffraction (XRD) and cross-sectional transmission electron microscopy (XTEM) have been adopted to obtain structural information about the multilayer structures. It may be noted that to form a multilayer with smooth interface, the layer should be either amorphous or epitaxial. This can be understood as following. Epitaxial films are grown layer-by-layer and hence the interfaces are atomically sharp, whereas the amorphous layers tend to heal the roughness of the underlying film. The amorphous layers are mostly used for the study of X-ray optics multilayers. This is because of the fact that the large difference in lattice spacing and structure between materials makes it difficult in obtaining the epitaxial films [16]. Whereas, the film growth follow Volmer-Weber growth (island) mode [16] and in this growth mode, each film tends to grow on the other as 3-D clusters rather than as a flat film.

Recently, Bosgra et al., using X-ray photoelectron spectroscopy sputter depth profiling studied the Inter-diffusion of a few nanometers thick C layer with Mo and Si under annealing at a temperature of 600 °C and reported that one can improve the thermal stability of Mo/Si mirrors by depositing a Si/C/Mo₂C/C/Si layer structure [17]. I. Nedelcu et al., studied the growth behavior of B₄C interlayers deposited at the interfaces of Mo/Si multilayers using x-ray photoemission spectroscopy, XRR and XRD measurements and reported that there exists an asymmetry in the formation of B₄C at the B₄C on Mo interface compared to the B₄C on Si interface [18]. Thanh-hai Nguyen et al., have reported the preparation and the parabolic, multilayer x-ray mirror (W/Al multilayers) that can be used with a general lab-based x-ray source and the effects of mirror on x-ray images were investigated using calculated modulation transfer function [19]. S. M. Al-Marzoug et al., reported the optimization of Pt/C based mirrors for the hard X-ray
region at different grazing angles using Luus-Jaakola optimization procedure [20]. Yu. A. Vainer et al., have developed a method using resonance diffuse x-ray scattering (that takes the occurrence of a mixed layer at the layer interfaces into account for the calculation of the intensity of diffusely scattered waves) to investigate the properties of W/B₄C multilayers with ultra-short periods (d= 0.7–1.5 nm)[21].

Based on the considerations as mentioned above, elements such as C, Si, B etc., are the mostly commonly used spacers with metallic layers as they grow amorphously and thereby tend to smoothen the interfaces. In the following sections, the main results reported in the literature on metal/Si and metal/C multilayer systems are summarized [22].

### 1.5.1 Metal/Silicon Multilayer System

There is considerable amount of work reported on metal/Silicon systems deposited mainly using sputtering and electron beam evaporation techniques [23-25]. Mo/Si and W/Si are the most well-studied systems. Many research groups have studied the performance of these multilayers with Si as the spacer layer in combination with different metals for high reflectivity and high thermal stability applications. The formation of amorphous silicide layer is reported and well established in the sputter and evaporated Metal/Si multilayers. Also, for example in Mo/Si multilayer, it is reported that the interlayer is thicker at the Mo-on-Si interface as compared to the Si-on-Mo interface and is explained in terms of higher momentum of the depositing Mo atoms as compared to the depositing Si atoms [26]. Holloway et al., [27] have reported the formation of MoSi₂ phase at the interface due to the crystallisation of the amorphous interlayer with the thermal annealing of Mo/Si multilayers using cross sectional TEM. It is reported that the formation of this phase hinders the solid state amorphization process and causing the contraction of bilayer periodicity as
measured from x-ray measurements. The changes in the periodicity of the structures are shown to affect the dispersing property of the multilayers and therefore, the multilayers can be used only up to a certain temperature depending on the constituent elements. After a certain temperature, the multilayer structure is destroyed. For example, for W/Si it reported that the multilayer structure is stable up to a temperature of only 773 K [28].

For the case of Mo/Si multilayers, significant changes in the interfacial properties are reported based on the preparation method. For example, it is reported that interfacial roughness is considerably higher for the films prepared with e-beam evaporation as compared to sputter deposited multilayers. These observations are explained in terms of lower kinetic energy of the adatoms which provides very less mobility for the adatoms on the substrate. In order to provide additional kinetic energy to the adatoms, grazing incidence ion bombardment has been used successfully in literature [29]. Schlatmann et al. [30] have used low energy Kr ions at grazing incidence to remove an excess layer of 0.5 nm from each layer of the Mo/Si multilayer structures and shown that this method results in smoothening of the interfaces. Similarly, other efforts such as thermal evaporation of multilayers on substrates kept at high temperatures etc., are shown to result in smoothening of the boundaries. Kloidt et al. [31] have studied the evaporation of Mo/Si multilayers on substrates kept at room temperature and at 423 K. They have observed that the multilayers deposited on heated substrates have considerably lower interfacial roughness as compared to that of room temperature. I. V. Kozhevnikov et al., reported the study of depth-graded (aperiodic) W/Si and W/B₄C mirrors with a period changing over depth and concluded that the mirrors with sharp interfaces (for example WSi₂/Si) are preferential for practical purposes [22, 32].
1.5.2 Metal /Carbon Multilayer System

Other multilayer that is extensively studied in the literature in the context of x-ray optics is W/C multilayer. Studies on a large number of metal/carbon systems (metal = W, Mo, Ru, Ni, Pt, Co) have been carried out by various research groups [5, 33, 34].

Unlike, Metal/Silicon systems period expansion is observed for the Metal/Carbon multilayers with thermal annealing. This is explained in terms of combined effects of expansion of carbon layers due to transformation to more of a graphitic microstructure, agglomeration of metal layers and formation of metal carbide phases. Thermal stability of W/C multilayer to temperatures as high as 1073 K, with a period expansion of about 10% are reported by Jiang et al [35]. High temperature annealing is found to destroy the layer structure because of tungsten carbides formation and agglomeration of tungsten layers. Various commercial firms are supplying the W/C multilayer mirrors as per the requirement and because of their high thermal stability, they are used as power filters in high power SR environment.

The thermal stability and the period expansion are strongly dependent on the factors such as the preparation method used, metal element etc. For example a period expansion of 18% after annealing at 623K is reported for Ni/C films prepared with PLD as compared to only about 4% for the films prepared by electron beam evaporation and the differences are explained in terms of density of carbon films [36, 37]. In the case of Pt/C multilayers, no carbide phase formation has been reported, which is explained in terms of noble nature of Pt. Due to the agglomeration of metal layers, usually the layer structure is destroyed after annealing at 673 K [38]. Co/C multilayers are also reported to be stable only up to a temperature of 723 K and have very large period expansion of 18% [22, 39].
1.6 Thermal Stability of Multilayers

It was studied in the literature that with increasing the temperature of the multilayer interdiffusion takes place at the interfaces and deteriorates the multilayer structure. Therefore it is also important to evaluate diffusion length with increasing annealing temperature. As mentioned above that any interdiffusion at the interfaces of the constituent layers can severely deteriorates the reflectivity at Bragg peak, resulting in loss of reflected intensity.

Therefore, many ideas were proposed to increase the stability of Metal/Si multilayers so that one can use them at higher working temperatures. One such idea was to use pairs of materials in thermodynamic equability [40], doping of metals with Si. With this the driving force of the Si diffusion into the metal is found to decrease and as a result the thermal stability increases. The enhancement of working temperature from 873 K to 1073 K is observed for MoSi$_2$/Si multilayers [41]. However, the disadvantage is a reduced reflectivity due to the decrease of composition gradient [6, 22].

1.6.1 Use of Diffusion Barrier

Generally in order to improve the thermal stability, what is used is known as diffusion barrier in mirrors. They reduce silicide formation due to interdiffusion of the metal/Si interfaces, increase reflectance and increase thermal stability. Deposition of thin barrier layer is shown to be effective in improving the properties of x-ray mirrors. For example, about 0.5nm carbon layer deposition between the two layers of a multilayer i.e., between Mo and Si, thus resulting in Mo/C/Si/C is shown to improve the thermal stability considerably and also without affecting the optical performance [42]. Similarly, elements such as W, Cr, B$_4$C etc., are used as diffusion barrier layers to optimize the thermal stability, optical properties of the mirrors in literature. W layer has been used as diffusion barrier layer to improve the thermal stability (up to
of Sc/Si multilayer mirrors [43], however the reflectivity was found to be poor due to the absorption of W. With about 0.3 nm thick Cr layer, the temperature range is found to be only 423 K, with boron carbide the temperature range was 573K. Coming to the Mo/Si mirrors, many elements are used at the interfaces to enhance multilayer stability. Techniques such ion implantation are also used to enhance the optical properties of mirrors. Implantation of CH$^+$ ions so that C gets implanted into Si layers is shown to affect the both reflectivity and multilayer period up to 423 K [44]. The deposition of Mo2C at the interfaces is reported to increase the reflectivity [45]. The addition of sub-nanometer thick B4C layers at the interfaces of Mo/Si multilayers has been shown to enhance the reflectivity and stability of multilayers as well [22, 46, 47].

1.7 Motivation and Scope of the Present Work

The present thesis deals with various issues that are related with the stability of x-ray mirror, considering the W/Si multilayer as a model system. W/Si multilayer are one of the most common systems which are used for both soft and hard x-ray regime applications. When the x-ray optics are subjected to high power, the thermal stability of the multilayer mirror to be ensured and one can summarize the problem that are expected when such multilayer structures are exposed to high heat loads: (i) Interdiffusion of the constituent elements (ii) Increase in the interfacial roughness due to agglomeration of the metal layers (iii) Compounds formation at the interface etc., which eventually destroy the periodic nature of the multilayer structure and hence are to be avoided from an a application point of view. Apart from the application point of view, study of the kinetic and thermodynamic aspects in the interdiffusion and interfacial reactions in multilayer structures, which are basically grown under non-equilibrium conditions are also of interest from basic physics point of
view. Therefore, techniques which are non-destructive to study the surfaces and interfaces at atomic level are essential in order to understand and evaluate the performance of a given multilayer structures. Silicon and carbon are the frequently used spacer layers in combination with refractory metals as it forms amorphous layers and hence making the interfaces smoother.

During use of x-ray multilayers with synchrotron radiation sources, the multilayer can get heated substantially by intense x-ray pulse falling on it. Therefore thermal stability of these multilayers at elevated temperature is also of significance. In the present thesis various issue related to the thermal stability of this multilayer has been addressed by taking the W/Si and W/B₄C/Si/B₄C as the samples.

The samples are prepared with ion beam sputtering method. It is important to have a suitable chamber, vacuum conditions etc., for the preparation of good quality multilayers. We have carried out XRR measurements extensively in the present work on the prepared samples. The important contribution of the present work is the XRR measurements of the prepared samples using in-situ methods, as mentioned below. The following are the objectives / aims of the present thesis work:

1. Design and development of a deposition chamber suitable for the preparation of high quality multilayer mirrors.
2. Thermal stability of W/Si multilayer has been studied in detail and the activation energy for interdiffusion at the interface has been estimated. Once the activation energy and the pre-exponential factor for the interdiffusion are known, long term stability of the multilayer at any given temperature can be estimated accurately. In-situ x-ray reflectivity measurements at elevated temperatures have also been done in order to get a deeper insight into the mechanism of deterioration of multilayers. It is found that stress generated due to unequal thermal expression of the
substrate and different layers is one of the main cause of deterioration in the reflectivity.

3. Role of B₄C as diffusion barrier in order to increase the thermal stability of the W/Si multilayer mirror has been studied. In view of the poor x-ray contrast between Si and B₄C, in this particular case, neutron reflectivity is used to study these mirrors.

4. A controlled modification of interfaces in W/Si multilayer mirror has been achieved by irradiation the multilayer mirror with swift heavy ions. Such a controlled modification of the interfaces may be needed for designing multilayer mirror for use as monochromators with reduced higher harmonics contain. This study also provided interesting information about the swift heavy ion induced intermixing in system with positive heat of mixing. Most of the studies in this aspect are carried out using ex-situ irradiation. In the present work, we have done the in-situ XRR measurements of the multilayer mirrors with swift heavy ion irradiation.
References:

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